165. *Syntheses in the Phenanthrene Series. Part X.* 8-*Methoxy*-1-*methylphenanthrene.*

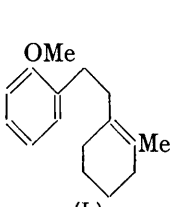
By J. Lockett and W. F. Short.

The product previously obtained (Part VIII) from 1-β-*o*-anisylethyl-2-methyl-*cyclo*hexene (I) is not 8-*methoxy*-1-*methylphenanthrene*. This compound has now been synthesised from 1-β-o-*anisylethyl*-2 : 6-*dimethyl*cyclo*hexene* (IV).

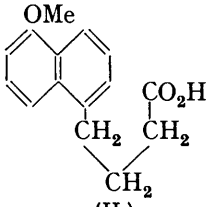
In Part VIII (J., 1937, 1619) it was stated that 1-β-*o*-anisylethyl-2-methyl*cyclo*hexene (I) could be converted into 8-methoxy-1-methylphenanthrene (m. p. 96—97°; picrate, m. p. 141·5—142·5°) by the successive action of aluminium chloride and sulphur. A small yield of a picrate, which did not depress the m. p. of that obtained by this method, was obtained from the product of the action of methylmagnesium iodide and sulphur on the ketone $C_{15}H_{14}O_2$, m. p. 88—89°, prepared by the dehydration of γ-5-methoxy-1-naphthylbutyric acid (II). This ketone was therefore considered to be 1-keto-8-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene. The necessity for a revision of this work became apparent when it was found (Part IX; J., 1938, 694) that the principal product obtained by cyclisation and dehydrogenation of 1-β-*p*-anisylethyl-2-methyl*cyclo*hexene (III) was 3-methoxyphenanthrene.

We have now prepared 1-β-o-*anisylethyl*-2 : 6-*dimethyl*cyclo*hexene* (IV) and find that on cyclisation and dehydrogenation it affords 8-*methoxy*-1-*methylphenanthrene*, m. p. 117·5—118° (*picrate*, m. p. 151—152°). γ-5-Methoxy-1-naphthylbutyric acid (II) has been prepared both from coumarin *via* 1-*keto*-5-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (V) and γ-5-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylbutyric acid* (VI) and from 5-hydroxy-1-

naphthylamine, through 1-*iodo*-5-*methoxynaphthalene* and β-5-methoxy-1-naphthoylpropionic acid. Cyclisation of the acid invariably afforded the ketone, m. p. 88—89°, although Kon and Ruzicka (J., 1936, 187) obtained from it an additional isomeric ketone, m. p. 137°. The successive action of methylmagnesium iodide and sulphur on the ketone of lower m. p. afforded a compound, the picrate of which melted somewhat higher than that previously obtained, and analysis of the parent *compound*, m. p. 105—106°, showed that it



(I.)



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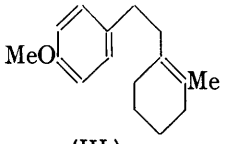

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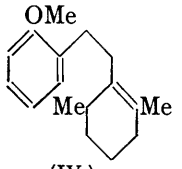
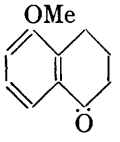
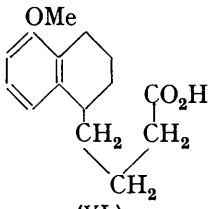


(IV.)

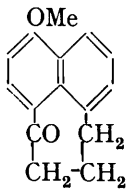
cannot be a methoxymethylphenanthrene. We therefore suggested that the ketone, m. p. 88—89°, must be 7-*keto*-4-*methoxy*-7 : 8-*dihydrohomophenalene* (VII), a structure which harmonises better with its fission by hydrobromic acid to γ-5-hydroxy-1-naphthylbutyric acid (Part VIII) and has been shown to be correct by Kon and Soper (following paper). Specimens of 8-methoxy-1-methylphenanthrene and its picrate prepared by Kon and Soper (*loc. cit.*) from the isomeric ketone, m. p. 137°, caused no depression in m. p. on admixture with our preparations from 1-β-*o*-anisylethyl-2 : 6-dimethyl*cyclo*hexene. The ketone, m. p. 137°, must therefore be 1-keto-8-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene as originally suggested by Kon and Ruzicka (*loc. cit.*).



(V.)



(VI.)



(VII.)

Experimental.

1-β-o-*Anisylethyl*-2: 6-*dimethyl*cyclo*hexan*-1-*ol*.—2 : 6-Dimethyl*cyclo*hexanone, prepared either from ethyl 2-methyl*cyclo*hexanone-6-carboxylate (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1163) or by the oxidation of 2 : 6-dimethyl*cyclo*hexanol (Skita, *Ber.*, 1923, **56**, 2241), was purified through the oxime (Wallach, *Annalen*, 1912, **397**, 200). Addition of the ketone to a cold Grignard solution prepared from β-*o*-anisylethyl chloride (J., 1937, 1620) afforded the tertiary *alcohol* as a viscous liquid, b. p. 185°/3·5 mm. (Found: C, 78·1; H, 10·0. $C_{17}H_{26}O_2$ requires C, 77·9; H, 9·9%), and dehydration of this with potassium hydrogen sulphate yielded 1-β-o-*anisylethyl*-2 : 6-*dimethyl*cyclo*hexene* (IV), b. p. 165—168°/7 mm. (Found: C, 83·2; H, 9·9. $C_{17}H_{24}O$ requires C, 83·6; H, 9·8%).

8-*Methoxy*-1-*methylphenanthrene*, obtained by treatment of (IV) with aluminium chloride and dehydrogenation with sulphur, separated from methyl alcohol in stout needles, m. p. 117·5—118° (Found: C, 86·3; H, 6·1. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). The *picrate* separated from alcohol in orange-red needles, m. p. 151—152° (Found: C, 58·45; H, 3·55; N, 8·9. $C_{16}H_{14}O,C_6H_3O_7N_3$ requires C, 58·5; H, 3·8; N, 9·3%). Admixture of the phenanthrene and its picrate with the products obtained by Kon by an alternative synthesis (following paper) caused no depression in m. p.

5-*Methoxy*-1-*naphthylamine*.—Acetylation of 5-hydroxy-1-naphthylamine with acetic anhydride (5 mols.) at room temperature and crystallisation of the product from chloroform gave 5-*acetamido*-1-*naphthol*, m. p. 176—177°, in 83% yield (Found: C, 71·4; H, 5·7. $C_{12}H_{11}O_2N$ requires C, 71·6; H, 5·7%). Methylation at 0—20° with methyl sulphate (1·3 mols.) and 2·8% sodium hydroxide solution (1·2 mols.) afforded the *methyl* ether, which separated from alcohol in colourless plates, m. p. 189—190° (Found: C, 72·6; H, 5·9. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·05%). Yield, 66%. The acetyl group was removed from the preceding

compound (100 g.) by boiling for 2 hours with alcohol (750 c.c.) and concentrated hydrochloric acid (200 c.c.). 5-*Methoxy*-1-*naphthylamine*, isolated in the usual way, crystallised from methyl alcohol in colourless prisms, m. p. 80—81° (Found : C, 75·95; H, 6·5. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·4%). Yield, 80%.

1-*Iodo*-5-*methoxynaphthalene*.—A 57% yield of this *iodo*-compound was obtained from 5-methoxy-1-naphthylamine by diazotisation and reaction with potassium iodide. It was purified by distillation, b. p. 165—175°/6 mm., and crystallisation from alcohol, from which it separated in cream plates, m. p. 79—80° (Found : C, 46·6; H, 3·4. $C_{11}H_{11}OI$ requires C, 46·5; H, 3·2%).

β-5-*Methoxy*-1-*naphthoylpropionic Acid*.—The reaction between a Grignard solution prepared from the preceding iodo-compound and succinic anhydride under the conditions described in the case of the corresponding bromo-compound (J., 1937, 1621) afforded β-5-methoxy-1-naphthoylpropionic acid, m. p. 153—154°, in 29% yield.

γ-o-*Anisylpropyl Alcohol*.—(1) Reduction of coumarin with sodium and ethyl alcohol (Semmler, *Ber.*, 1906, **39**, 2855) or amyl alcohol (v. Auwers, *Annalen*, 1918, **415**, 152) afforded γ-2-hydroxyphenylpropyl alcohol, b. p. 176—178°/12 mm., in 53 and 45% yield respectively. Methylation of the alcohol in 10% sodium hydroxide solution (1·4 mols.) with methyl sulphate (1·4 mols.) gave an 82% yield of γ-*o*-anisylpropyl alcohol, b. p. 145—146°/10 mm., which was characterised as its 3 : 5-*dinitrobenzoate*, m. p. 113—114° (Found : C, 56·7; H, 4·5. $C_{17}H_{16}O_7N_2$ requires C, 56·7; H, 4·4%).

(2) Methylation of coumarin as described by Reimer and Howard (*J. Amer. Chem. Soc.*, 1928, **50**, 197) gave methyl *O*-methylcoumarinate, b. p. 150—163°/10 mm., and *o*-methoxycinnamic acid, m. p. 86—87°, in 69 and 13% yield respectively. Catalytic reduction of the ester furnished methyl β-*o*-anisylpropionate, b. p. 146—147°/10 mm., in quantitative yield and reduction of the acid afforded β-*o*-anisylpropionic acid (m. p. 85·5—86°; yield, 80%), from which a 50% yield of ethyl β-*o*-anisylpropionate, b. p. 140—155°/10 mm., was obtained with 10% alcoholic hydrogen chloride. The two esters were reduced with sodium (6 atoms) and absolute alcohol (28 mols.), γ-*o*-anisylpropyl alcohol, b. p. 145—146°/10 mm., being obtained in 62% yield.

γ-o-*Anisylbutyric Acid*.—The preceding alcohol was converted into γ-*o*-anisylpropyl chloride, b. p. 120—130°/10 mm., by the action of thionyl chloride and dimethylaniline or pyridine, the yields being 55 and 80% respectively. An 80% yield of the corresponding nitrile, b. p. 135—145°/12 mm., was obtained from the chloride and alcoholic potassium cyanide in presence of sodium iodide and copper sulphate. Hydrolysis of the nitrile with methyl-alcoholic potassium hydroxide furnished γ-o-*anisylbutyric acid*, m. p. 39—39·5° (Found : C, 68·0; H, 7·5. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). The yield of the acid was 60% and a small quantity of neutral by-product, b. p. 120—122°/10 mm. (Found : C, 73·2; H, 9·1. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%), was shown to be γ-o-*anisylpropyl methyl ether* by oxidation to *O*-methysalicylic acid, m. p. and mixed m. p. 99—100°.

1-*Keto*-5-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—Ring closure of the preceding acid with phosphoric oxide–benzene produced the ketone in 16% yield, and after numerous trials with sulphuric acid and stannic chloride the following method was devised. Phosphorus oxychloride (5 c.c.) was added drop by drop to a solution of the acid (10 g.) in tetrachloroethane (200 c.c.), and the mixture boiled for 2½ hours. The *ketone*, isolated in the usual way, separated from light petroleum (b. p. 40—60°) in white plates, m. p. 89—89·5° (Found : C, 75·0; H, 6·8. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·7%). Yield, 55%. The semicarbazone melted at 249—250°.

β-(5-*Methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*)*ethyl Alcohol*.—A 75% yield of ethyl 5-methoxy-3 : 4-dihydro-1-naphthylacetate, b. p. 160—175°/0·6 mm., was obtained from the cyclic ketone by the Reformatsky reaction, followed by dehydration with phosphoric oxide. Reduction of the unsaturated ester with sodium (7 atoms) and absolute alcohol (15 mols.) gave a 61% yield of the alcohol, b. p. 160—175°/0·6 mm., and a small amount of 5-methoxy-1 : 2 : 3 : 4-tetrahydronaphthylacetic acid, m. p. 146—147°, was isolated as a by-product. The alcohol was characterised as the 3 : 5-*dinitrobenzoate*, which separated from ligroin in slightly yellow, clustered needles, m. p. 107—108° (Found : C, 59·8; H, 5·2. $C_{20}H_{20}O_7N_2$ requires C, 60·0; H, 5·0%).

γ-(5-*Methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*)*butyric Acid*.—A solution of phosphorus tribromide (3·4 c.c.) in chloroform (28 c.c.) was added below 5° with mechanical stirring to a mixture of the preceding alcohol (20 g.), dimethylaniline (4·6 c.c.), and chloroform (50 c.c.) and, after standing for 12 hours at room temperature, the bromide was isolated in the known manner. Yield, 62%. The crude bromide, which could not be distilled without decomposition, was

heated at 120—130° for 60 hours with ethyl potassiomalonate (from 1·7 atoms of the metal and 2·0 mols. of ester) suspended in dry toluene. The malonic ester so obtained (yield, 65%) was hydrolysed to β-(5-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*)*ethylmalonic acid*, m. p. 124—126° (Found : C, 66·0; H, 6·7. $C_{16}H_{20}O_5$ requires C, 65·8; H, 6·8%). Yield, 85%. Decarboxylation was effected by heating at 190—210° for 2 hours and the resulting γ-(5-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*)*butyric acid* crystallised from light petroleum in plates, m. p. 67—68° (Found : C, 72·3; H, 8·1. $C_{15}H_{20}O_3$ requires C, 72·6; H, 8·1%). Yield, 95%.

γ-(5-*Methoxy*-1-*naphthyl*)*butyric Acid.*—(1) Reduction of β-5-methoxy-1-naphthoylpropionic acid by Clemmensen's method, the technique previously described (J., 1937, 1621) being used, afforded γ-(5-methoxy-1-naphthyl)butyric acid, m. p. 143°, in 58% yield. (2) Dehydrogenation of γ-(5-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthyl)butyric acid with sulphur (2 atoms) at 190—210° for 5 hours gave the same acid, m. p. 141—142°, in 50% yield.

Dehydration of γ-(5-*Methoxy*-1-*naphthyl*)*butyric Acid.*—Dehydration of the acid either with phosphoric oxide–benzene or with stannic chloride invariably gave the same ketone, m. p. 88—89°, the average yields being 47% and 39% respectively. The m. p. of the semicarbazone, 227—228°, was somewhat higher than the value previously recorded (J., 1937, 1621) (Found : C, 67·7; H, 5·9. Calc. : C, 67·8; H, 6·0%). Interaction between the cyclic ketone and methylmagnesium iodide, followed by dehydrogenation with sulphur, afforded, in addition to some unchanged ketone, a trace of a *compound*, m. p. 105—106° (picrate, m. p. *ca.* 157°), which cannot be a methoxymethylphenanthrene (Found : C, 75·0; H, 5·4. Calc. for $C_{16}H_{14}O$: C, 86·5; H, 6·3%).

The compounds designated 1-keto-8-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (m. p. 88—89°) and 8-methoxy-1-methyl-3 : 4-dihydrophenanthrene (m. p. 104—105°) in Part VIII (*loc. cit.*, p. 1621) should now be named 7-*keto*-4-*methoxy*-7 : 8-*dihydrohomophenalene* (VII) and 4-*methoxy*-7-*methylhomophenalene* respectively.

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