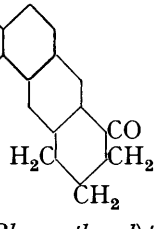
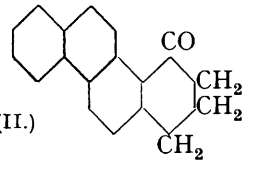
238. *A New Route to Chrysene and* 1 : 2-*Benzanthracene.*

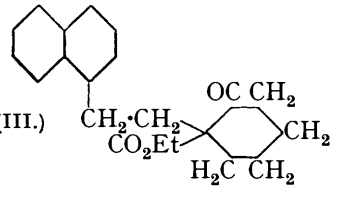
By Robert D. Haworth and Cecil R. Mavin.

With the object of devising reactions for the synthesis of benzophenanthrenes, the condensation of succinic anhydride and phenanthrene in the presence of aluminium chloride has been investigated.

β-(3-*Phenanthroyl*)*propionic acid*, contaminated with a trace of inseparable isomeride, was obtained in 60% yields, and the structure of this acid was established by an independent synthesis from 3-phenanthryl methyl ketone (Mosettig and van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704). The ω-bromo-derivative of this ketone reacted with ethyl sodiomalonate and the product, after hydrolysis and heating, yielded β-(3-phenanthroyl)propionic acid. This keto-acid, reduced by Clemmensen's method, gave γ-(3-*phenanthryl*)*butyric acid*, which was converted into 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-5 : 6-*benzanthracene* (I) by the action of 85% sulphuric acid. Much sulphonation occurred during this ring closure, but no evidence was obtained of the formation of the 4-keto-isomeride. The cyclic ketone (I) was reduced by Clemmensen's method and the product dehydrogenated with selenium to yield 1 : 2-benzanthracene.

(I.) 

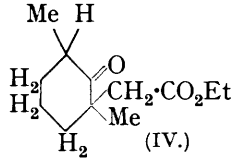
(II.) 

(III.) 

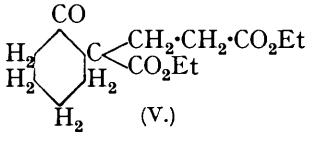
β-(2-*Phenanthroyl*)*propionic acid* has been prepared from 2-phenanthryl methyl ketone (Mosettig and van de Kamp, *loc. cit.*) by condensing the ω-*bromo*-derivative with ethyl sodiomalonate and hydrolysing and heating the product. The keto-acid was reduced to γ-(2-*phenanthryl*)*butyric acid* which was cyclised with 85% sulphuric acid. There was evidence that this ring closure occurred in two directions, for although the crude cyclic ketone gave correct analytical figures, a pure specimen of 7-*keto*-4 : 5 : 6 : 7-*tetrahydrochrysene* (II)* was obtained only after repeated crystallisation. When this ketone was reduced

* The numbering of the ring is that of Ramage and Robinson (this vol., p. 608); it differs from Beilstein's supplement (new edition) in that the latter would number it 6-keto-3 : 4 : 5 : 6-tetrahydrochrysene.

with amalgamated zinc and hydrochloric acid, an amorphous product was obtained which was readily dehydrogenated with selenium to yield chrysene. According to the earlier views of Rosenheim and King (*J. Soc. Chem. Ind.*, 1932, **51**, 956), the hydrocarbon, $C_{18}H_{16}$, obtained from sterols and the bile acids, may be identical with 1 : 2 : 3 : 4-tetrahydrochrysene, but the ease of hydrogenation of the amorphous product, mentioned above, does not support this view. Dr. Rosenheim (private communication) has suggested that the phenanthrene nucleus may be reduced by the Clemmensen process, and that the amorphous product may actually be a hexahydrochrysene. This view is contrary to general experience with the reduction of such cyclic ketones, which usually give rise to the corresponding tetrahydro-derivative along with substances of higher molecular weight. We have now shown that 2- and 3-phenanthryl methyl ketones may be converted into 2- and 3-*ethylphenanthrenes* respectively, without nuclear reduction, by this method, and in our opinion the amorphous product is largely composed of 4 : 5 : 6 : 7-tetrahydrochrysene.



(IV.)



(V.)

$HO_2C \cdot (CH_2)_4 \cdot CH \cdot (CH_2)_2 \cdot CO_2H$
CO_2H
(VI.)

The method employed by Bardhan and Sengupta (J., 1932, 2520, 2798) for the synthesis of phenanthrene derivatives has been extended to the synthesis of chrysene. β-1-Naphthylethyl alcohol, prepared by the action of ethylene oxide on 1-naphthylmagnesium bromide, was converted into the corresponding *bromide*, which reacted with ethyl potassio*cyclo*hexanone-2-carboxylate to yield *ethyl* 2-(β-1′-*naphthylethyl*)-cyclo*hexanone-2-carboxylate* (III). This ester underwent ketonic hydrolysis and ring closure with 85% sulphuric acid, yielding an oil which was converted into chrysene by dehydrogenation with selenium.

Several unsuccessful attempts have been made to utilise 1-keto- and 1 : 3-diketo-1 : 2 : 3 : 4-tetrahydrophenanthrene for the synthesis of chrysene and *cyclo*pentenophenanthrene. These ketones were unattacked by treatment with ethyl succinate, ethyl acetoacetate, or ethyl glutarate in the presence of sodium, sodium ethoxide, or sodamide. Despite the fact that 2 : 6-dimethyl*cyclo*hexanone reacted with ethyl bromoacetate in the presence of sodamide to give *ethyl* 2 : 6-*dimethyl*cyclo*hexanone-2-acetate* (IV), attempts to condense 1-keto- or 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene with ethyl bromoacetate or β-bromopropionate were unsuccessful.

Preliminary experiments with ethyl *cyclo*hexanone-2-carboxylate suggested a possible method for the synthesis of polycyclic systems. The sodio-derivative of this ester reacted readily with ethyl β-bromopropionate to give *ethyl* 2-*carboxy*cyclo*hexanone*-2-β-*propionate* (V), which on hydrolysis gave a mixture of cyclo*hexanone*-2-β-*propionic acid* and *heptane*-1 : 3 : 7-*tricarboxylic acid* (VI), but our failure to prepare ethyl 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-carboxylate has precluded the application of similar reactions.

Experimental.

Bromomethyl 2-Phenanthryl Ketone.—Bromine (2·3 c.c.) in chloroform (10 c.c.) was added gradually to a cold solution of 2-phenanthryl methyl ketone (9·7 g.) in chloroform (160 c.c.), the flocculent yellow addition compound decomposed by gentle warming, and the product set aside for 12 hours. The hydrogen bromide was removed in a current of dry air, the chloroform in a vacuum, and the residue crystallised from benzene (charcoal); the *bromo-ketone* (9·7 g.) was obtained in stout colourless prisms, m. p. 140—142° (Found: Br, 26·5. $C_{16}H_{11}OBr$ requires Br, 26·8%). Bromomethyl 3-phenanthryl ketone, prepared similarly, was a viscous oil.

β-(3-*Phenanthroyl*)*propionic acid* was obtained by two methods. (*a*) 45% Yields were achieved by adding a solution of bromomethyl 3-phenanthryl ketone (9·7 g.) in benzene to a suspension of ethyl sodiomalonate (from granulated Na, 1·15 g., and ethyl malonate, 8 g.) in benzene (40 c.c.) and boiling the mixture for 12 hours. Dilute sulphuric acid was then added, the benzene removed, and the viscous residue hydrolysed by 1 hour's boiling with methyl-alcoholic potash (130 c.c. of 10%). Water (100 c.c.) was added, the alcohol removed, the

solution filtered (charcoal), and the residue extracted several times with boiling water. The united extracts were acidified, the light brown granular mass collected, heated for 1 hour at 180—185°, and purified by solution in sodium carbonate solution (charcoal), filtration, and precipitation. (*b*) 60% Yields were obtained by adding succinic anhydride (11 g.) with cooling to a mixture of phenanthrene (17·8 g.), anhydrous aluminium chloride (30 g.), and nitrobenzene (130 c.c.). After 2 days, dilute hydrochloric acid was added, the nitrobenzene removed in steam, and the semi-solid residue crystallised from acetic acid. β-(3-Phenanthroyl)propionic acid, prepared by methods (*a*) and (*b*), crystallised from methyl alcohol, acetic acid, or benzene in colourless slender prisms, m. p. 157—158° (Found : Equiv., 276. $C_{18}H_{14}O_3$ requires equiv., 278) and 147—149° (Found : Equiv., 277·5) respectively. The acids obtained by the two methods are essentially identical for the following reasons : (1) they had mixed m. p. 147—149°, (2) both yielded the same *oxime*, which crystallised from methyl alcohol in slender colourless prisms, m. p. 169—170° (decomp.) (Found : N, 5·0. $C_{18}H_{15}O_3N$ requires N, 4·8%), (3) both were oxidised by sodium hypochlorite to phenanthrene-3-carboxylic acid, m. p. 276—278°, which was converted into the ethyl ester, m. p. 55—57° (cf. Mosettig and van de Kamp, *loc. cit.*), and (4) both were reduced to γ-(3-phenanthryl)butyric acid as described below. The acids prepared by methods (*a*) and (*b*) gave approximately equal yields in experiments (2), (3), and (4).

γ-(3-*Phenanthryl*)*butyric acid* was obtained in 50% yields, by gradually adding concentrated hydrochloric acid (8 vols.) to a boiling mixture of the keto-acid (1 part), glacial acetic acid (16 vols.), and amalgamated zinc (6 parts) during 3 hours. After boiling for a further 5 hours, the mixture was diluted with water, extracted with ether, washed free from acetic acid, dried, the solvent removed, and the residue crystallised from a small amount of benzene; small colourless prisms, m. p. 138—139°, were obtained (Found : Equiv., 262. $C_{18}H_{16}O_2$ requires equiv., 264).

1-*Keto*-1 : 2 : 3 : 4-*tetrahydro*-5 : 6-*benzanthracene* (I) was prepared in 40% yields by heating the above butyric acid (1 part), water (1 vol.), and concentrated sulphuric acid (3 vols.) at 100° for 50 minutes. The mixture was diluted with water, extracted with ether, the extract washed first with water and then with dilute ammonia, dried, the solvent removed, and the residue crystallised from much alcohol; colourless prisms, m. p. 179—180° (Found : C, 87·8; H, 5·9. $C_{18}H_{14}O$ requires C, 87·7; H, 5·7%). The alcoholic mother-liquors yielded a small amount of a compound which crystallised from alcohol or glacial acetic acid in pale buff-coloured needles, m. p. 246—248° (Found : C, 82·3; H, 5·1. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3%).

1 : 2-*Benzanthracene*.—1-Keto-1 : 2 : 3 : 4-tetrahydro-5 : 6-benzanthracene (1 g.) was reduced by Clemmensen's method and the product heated with selenium (1 g.) at 280—290° for 15 hours and then at 305—315° for a further 10 hours. The product, isolated with chloroform, was distilled over sodium under reduced pressure, and crystallised from alcohol or acetic acid; colourless plates, m. p. 155—157°. This hydrocarbon, its picrate, m. p. 142—143°, and quinone, m. p. 165—167°, were identified by comparison with authentic specimens.

β-(2-*Phenanthroyl*)*propionic acid* was prepared from bromomethyl 2-phenanthryl ketone in 45% yields, as described in method (*a*) for the preparation of β-(3-phenanthroyl)propionic acid. It crystallised from 90% acetic acid or alcohol in colourless slender prisms, m. p. 205—206° (Found : Equiv., 277).

γ-(2-*Phenanthryl*)*butyric acid*, obtained from the above keto-acid in 50% yields, as described for the preparation of γ-(3-phenanthryl)butyric acid, crystallised from 50% acetic acid or a small amount of benzene in glistening prisms, m. p. 134—135° (Found : Equiv., 265).

7-*Keto*-4 : 5 : 6 : 7-*tetrahydrochrysene* (II) was prepared as described for (I). The neutral, water-insoluble product, obtained in 60% yield, was once crystallised from alcohol; colourless prisms were obtained, m. p. 110—112° (Found : C, 87·9; H, 5·9%). After three further crystallisations from alcohol, large colourless prisms, with the constant m. p., 124—125°, were obtained (Found : C, 87·7; H, 5·9%). No homogeneous by-product was isolated from the mother-liquors.

β-1-*Naphthylethyl Alcohol*.—1-Naphthylmagnesium bromide, from 1-bromonaphthalene (20 g.) and magnesium (2·5 g.) in ether (50 c.c.), was cooled to −15°, and a solution of ethylene oxide (6 g.) in ether gradually added. After 24 hours, the ether was removed, the residue heated on a steam-bath for 2 hours, decomposed with dilute sulphuric acid, extracted with ether, and distilled under reduced pressure. β-1-Naphthylethyl alcohol (10 g.) was obtained, with properties described by Grignard (*Compt. rend.*, 1905, **141**, 45; *Ann. Chim.*, 1907, **10**, 30). β-1-*Naphthylethyl bromide* was prepared in 80% yield by boiling the alcohol with 40% hydrobromic acid (5 vols.) for 4 hours. The product was diluted with water, extracted with ether,

and distilled; a colourless liquid, b. p. 145—148°/0·3 mm., was obtained (Found : Br, 33·8. $C_{12}H_{11}Br$ requires Br, 34·0%).

Ethyl 2-(β-1′-*Naphthylethyl*)cyclo*hexanone-2-carboxylate* (III).—β-1-Naphthylethyl bromide (4·8 g.) was added to a suspension of ethyl potassio*cyclo*hexanone-2-carboxylate, prepared from powdered potassium (0·8 g.) and ethyl *cyclo*hexanone-2-carboxylate (3·4 g.), in dry benzene, and the mixture refluxed for 48 hours. After cooling, water was added, and the benzene layer separated, washed with dilute sodium hydroxide, and distilled. The *ester* (III) was obtained as a viscous liquid (2·9 g.), b. p. 210—215°/0·3 mm. (Found : C, 77·5; H, 7·0. $C_{21}H_{22}O_3$ requires C, 77·9; H, 6·8%).

Chrysene.—(*a*) 7-Keto-4 : 5 : 6 : 7-tetrahydrochrysene (0·9 g.) was reduced with amalgamated zinc (5 g.) and concentrated hydrochloric acid (5 c.c.). The product (0·8 g.), isolated with ether, was an amorphous powder, sparingly soluble in hot alcohol, and was dehydrogenated by heating with selenium (1 g.) at 290—310° for 24 hours. (*b*) The ester (III) (2 g.) was heated on the steam-bath for 1 hour with concentrated sulphuric acid (6 c.c.) and water (2 c.c.). Frothing occurred, and the deep green solution was diluted with water and extracted with ether. The extract was washed, first with water and then with dilute ammonia, dried, and distilled. The distillate (0·6 g.), b. p. 180—200°/0·3 mm., was dehydrogenated with selenium as described in (*a*). The product from (*a*) or (*b*) was extracted with chloroform, distilled over sodium under reduced pressure, and crystallised first from acetic acid and then from benzene; glistening leaflets, m. p. 251—252°. The quinone, m. p. 239°, and the addition compound with 2 : 7-dinitroanthraquinone, m.p. 298—299°, were prepared, and the hydrocarbon and derivatives were identified by comparison with authentic specimens.

2-*Ethylphenanthrene.*—A mixture of 2-phenanthryl methyl ketone (2 g.), amalgamated zinc (10 g.), and concentrated hydrochloric acid (10 c.c.) was boiled for 16 hours, diluted with water, extracted with ether, dried, and the solvent removed. The semi-solid, brown residue (X) was extracted several times with hot methyl alcohol (charcoal), in which it was only partly soluble; evaporation of the alcohol from the extract yielded an oil (0·85 g.), which solidified completely and crystallised from methyl alcohol in colourless, glistening leaflets, m. p. 64—65° (Found : C, 93·1; H, 6·9. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). The *picrate* crystallised from methyl alcohol in orange-yellow prisms, m. p. 92—93° (Found : N, 9·9. $C_{22}H_{17}O_7N_3$ requires N, 9·7%). The methyl alcohol-insoluble portion of (X) is a high-boiling substance of unknown structure, and as the same yield of 2-ethylphenanthrene was obtained by dehydrogenating (X) with selenium and distilling the product in a vacuum over sodium, it was concluded that (X) was free from hydrogenated phenanthrene derivatives.

3-Ethylphenanthrene, prepared similarly from 3-phenanthryl methyl ketone, was a colourless oil yielding a *picrate*, which crystallised from methyl alcohol in slender orange-red prisms, m. p. 117—118° (Found : C, 60·5; H, 4·0. $C_{22}H_{17}O_7N_3$ requires C, 60·7; H, 3·9%). The *styphnate* crystallised from methyl alcohol in orange prisms, m. p. 114—116° (Found : N, 9·5. $C_{22}H_{17}O_8N_3$ requires N, 9·3%).

Ethyl 2 : 6-*Dimethyl*cyclo*hexanone-2-acetate* (IV).—2 : 6-Dimethyl*cyclo*hexanone (3·1 g.), obtained by a method essentially similar to that of Kotz and Blendermann (*J. pr. Chem.*, 1913, **88**, 258), and sodamide (1·2 g.) were refluxed in dry ether for 6 hours. Ethyl bromoacetate (4 g.) was added, and the heating continued for 24 hours, after which water was added, and the ether separated, dried, and distilled. The *ester* (IV) (1·5 g.) was obtained as a colourless oil, b. p. 132—134°/15 mm. (Found : C, 68·2; H, 9·3. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·4%).

Ethyl 2-*Carboxy*cyclo*hexanone-2-β-propionate* (V).—Ethyl β-bromopropionate (17·2 g.) was added to a suspension of ethyl sodio*cyclo*hexanone-2-carboxylate, prepared from molecular sodium (2·7 g.) and ethyl *cyclo*hexanone-2-carboxylate (21 g.), in benzene (120 c.c.), and the mixture boiled for 12 hours. After addition of water, the benzene layer was washed with dilute sodium hydroxide solution, dried, and distilled under reduced pressure. The *ester* (V) (20 g.), b. p. 198—205°/15 mm., on redistillation gave a colourless oil, b. p. 199—202°/15 mm. (Found : C, 62·0; H, 8·3. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·1%).

cyclo*Hexanone-2-β-propionic Acid and Heptane*-1 : 3 : 7-*tricarboxylic Acid* (VI).—The ester (V) was boiled with 10% methyl-alcoholic potash (3 mols.) for 3 hours, and after dilution with water and removal of most of the alcohol, the residue was acidified, cooled, saturated with ammonium sulphate, and extracted several times with ether. The dried extract was distilled, giving (*a*) cyclo*hexanone-2-propionic acid*, b. p. 155—160°/0·2 mm., and (*b*) the *anhydride* of (VI), b. p. 250—260°/0·2 mm. Fraction (*a*) rapidly solidified, and crystallised from ether or ether–light petroleum (b. p. 40—60°) in colourless needles, m. p. 65—66° (Found : C, 63·9; H, 8·4; equiv., 167. $C_9H_{14}O_3$ requires C, 63·6; H, 8·2%; equiv., 170). The *methyl* ester

(prepared by use of methyl alcohol and concentrated sulphuric acid) was a colourless oil, b. p. 140—142°/15 mm. (Found : C, 64·9; H, 8·9. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%), which reacted with methylmagnesium iodide to give an oil, b. p. 155—160°/15 mm., having the properties of a lactone, and with ethyl bromoacetate and zinc to give an oil, b. p. 180—185°/15 mm., but these products have not been fully investigated. Fraction (*b*) solidified slowly to a hygroscopic mass, which crystallised from benzene in colourless nodules, m. p. 72—73° (Found : C, 55·9; H, 7·0; equiv., 70·6. $C_{10}H_{14}O_5$ requires C, 56·1; H, 6·6%; equiv., 71·3).

Our thanks are due to the Research Fund Committee of the Chemical Society for a grant, to Dr. J. W. Cook for specimens of chrysene and 1 : 2-benzanthracene, and to the Council of Armstrong College for a studentship which has enabled one of us to participate in this work.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.

[*Received, June 9th,* 1933.]