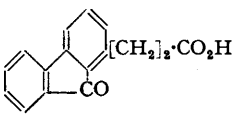
974. *New Derivatives of* 1 : 2-cyclo*Pentenophenanthrene.*

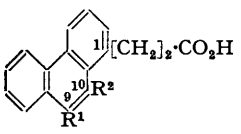
By G. M. Badger, W. Carruthers, and J. W. Cook.

Ring-expansion of β-9-keto-1-fluorenylpropionic acid (I) with diazomethane gave methyl β-9-methoxy-1-phenanthrylpropionate (as II) as the major product. The acid (II) was cyclised to 9-methoxy-7 : 8-benzoperinaphthan-1-one (VI). When the 10-position of (II) was blocked by chlorination cyclisation gave 10-chloro-3′-keto-9-methoxy-1 : 2-*cyclo*pentenophenanthrene (VIII). The oxidation of 1 : 2-*cyclo*pentenophenanthrene has been studied.

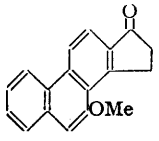
The ready availability of β-9-keto-1-fluorenylpropionic acid (I) by oxidation of tetrahydrofluoranthene (Kruber, *Ber.*, 1931, **64**, 84) suggested the use of this acid in a new route to derivatives of 1 : 2-*cyclo*pentenophenanthrene. 9-Methoxyphenanthrene has been obtained by the action of diazomethane on fluorenone (Schultz, Schultz, and Cochran, *J. Amer. Chem. Soc.*, 1940, **62**, 2902), so an analogous reaction with the acid (I) was expected to lead to methyl β-9-methoxy-1-phenanthrylpropionate (as II) or the isomeric 10-methoxy-compound (III). In the latter case the 10-methoxy-group would block cyclisation at this position and thus allow dehydration of (III) to 3′-keto-10-methoxy-1 : 2-*cyclo*pentenophenanthrene (V).



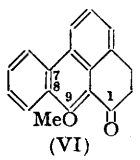
(I)



(II; R^1 = OMe, R^2 = H)
(III; R^1 = H, R^2 = OMe)
(IV; R^1 = OMe, R^2 = Cl)



(V)

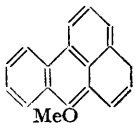


(VI)

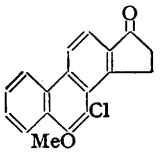
The crystalline ester isolated from the reaction products was evidently the 9-methoxy-compound, for cyclisation of the acid (II) which it furnished on hydrolysis gave 9-methoxy-7 : 8-benzoperinaphthan-1-one (VI). The corresponding carbinol, formed by catalytic hydrogenation or by reduction with lithium aluminium hydride, was converted into *meso*benzanthrone by hydrogen chloride in benzene. Presumably the dehydration product (VII) is an intermediate in this reaction and then readily undergoes demethylation to the corresponding phenol, which Bally and Scholl (*Ber.*, 1911, **44**, 1656) found to be readily oxidised to *meso*benzanthrone by atmospheric oxygen. Attempts to obtain additional support for the structure (VI) by reduction of this compound to the known 9-methoxy-1 : 10-trimethylenephenanthrene were unsuccessful; uncrystallisable gums were formed by the Clemmensen and the Huang-Minlon procedure.

In order to prevent cyclisation at position 10, the acid (II) was chlorinated with phosphorus pentachloride (cf. Autenrieth and Mühlinghaus, *Ber.*, 1906, **39**, 4098) to β-(10-chloro-9-methoxy-1-phenanthryl)propionic acid (IV). The chloride of this chloro-acid was cyclised by stannic chloride to 10-chloro-3′-keto-9-methoxy-1 : 2-*cyclo*pentenophenanthrene (VIII). The crude product of Clemmensen reduction of this ketone was oxidised by osmium tetroxide followed by chromic acid to 1 : 2-*cyclo*penteno-9 : 10-phenanthraquinone

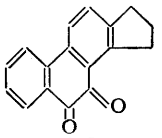
(IX), a compound previously obtained by Butenandt, Dannenberg, and von Dresler (*Z. Naturforsch.*, 1946, **1**, 222) by similar oxidation of the parent 1 : 2-*cyclo*pentenophenanthrene. Unsuccessful attempts were made to dehalogenate the chloro-ketone (VIII).



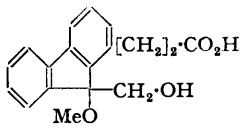
(VII)



(VIII)



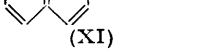
(IX)



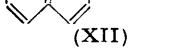
(X)

A subsidiary product of the action of diazomethane on the ketofluorenylpropionic acid (I) was a methyl ester, which was hydrolysed to an acid to which the structure (X) is assigned. The alcohol group was characterised by preparation of a 3 : 5-dinitrobenzoate from the ester, and the acid was oxidised by sodium dichromate in acetic acid to ketofluorenylpropionic acid (I). A compound such as (X) could arise from the methanolysis of the epoxide which is probably formed as an intermediate in the ring-expansion (cf. Mosettig and Burger, *J. Amer. Chem. Soc.*, 1930, **52**, 3456). Robinson and Smith (*J.*, 1937, 371) isolated a compound of similar type as a product of the reaction of *cyclo*hexanone and diazomethane.

A factor which was undoubtedly partly responsible for the delay in the identification of Diels's hydrocarbon, $C_{18}H_{16}$, from the dehydrogenation of cholesterol was its failure to undergo the chromic acid oxidation to an *o*-quinone which is normally characteristic of phenanthrene derivatives (Diels *et al.*, *Annalen*, 1927, **459**, 3). Cook and Hewett (*J.*, 1933, 1098) were likewise unable to obtain evidence of quinone formation by chromic acid oxidation of the parent 1 : 2-*cyclo*pentenophenanthrene, and attributed this to attack by the reagent of the five-membered ring. This reaction was re-examined by one of us in 1938, and it was found that oxidation of 1 : 2-*cyclo*pentenophenanthrene with chromic acid in cold acetic acid gave mainly 1′-keto-1 : 2-*cyclo*pentenophenanthrene (XI) together with a smaller amount of 1 : 2-*cyclo*penteno-9 : 10-phenanthraquinone (IX). Shortly afterwards Hoch (*Compt. rend.*, 1938, **207**, 921) reported the formation of the ketone (XI) by cold chromic acid oxidation of 1 : 2-*cyclo*pentenophenanthrene, and our own work was not pursued. More recently, however, Butenandt, Dannenberg, and Dresler (*loc. cit.*), evidently unaware of Hoch's work, reported that oxidation with chromic acid at 60° gave only a monoketone, which they suggested was (XI). Consequently, we now record our own experiments which led not only to the isolation of the quinone, but also to the definite identification of the ketone (XI) with the synthetic ketone of this structure prepared by Bachmann and Kloetzel (*J. Amer. Chem. Soc.*, 1937, **59**, 2207). We have also found that oxidation of 1 : 2-*cyclo*pentenophenanthrene with lead tetra-acetate gives 1′-acetoxy-1 : 2-*cyclo*pentenophenanthrene (XII; R = COMe); the hydroxy-compound (XII; R = H), formed by hydrolysis, was oxidised to the ketone (XI). The corresponding



(XI)



(XII)


(XIII)

benzoate, when heated with dimethylaniline, gave *cyclo*pentadienophenanthrene (XIII) (or the bond-isomer); this structure was for a time attributed mistakenly to two other compounds (cf. Cook and Hewett, *J.*, 1934, 365).

Experimental

1 : 2 : 3 : 4-*Tetrahydrofluoranthene*.—This was conveniently prepared in 85% yield by hydrogenation of fluoranthene (50 g.) in ethanol (800 c.c.) over a copper chromite catalyst (12 g.) at 95—100° and 130 atm. for 3 hours; it was oxidised to β-9-keto-1-fluorenylpropionic acid by sodium dichromate in acetic acid (Kruber, *Ber.*, 1931, **64**, 84).

Action of Diazomethane on β-9-Keto-1-fluorenylpropionic Acid (I).—The acid (I) (7·5 g.) was added to an ethereal solution (1 l.) of diazomethane prepared from methylnitrosourea (75 g.) (Arndt, *Org. Synth.*, 1935, **15**, 3). When the effervescence had ceased, methyl alcohol (1 l.) and a trace of sodium carbonate were added. After 5 days the solvent was removed under reduced pressure. A washed and dried benzene solution of the resulting orange gum was passed through a column of silica gel; elution with benzene afforded an eluate, fluorescing in ultra-violet light. Evaporation yielded a pale yellow oil (2·9 g.) which solidified when rubbed with light petroleum (b. p. 60—80°), giving *methyl β-9-methoxy-1-phenanthrylpropionate* as needles (from the same solvent), m. p. 71° (Found: C, 77·5; H, 6·1. $C_{19}H_{18}O_3$ requires C, 77·55; H, 6·1%). The *acid* (II) formed clusters of soft needles, m. p. 204° (from ethanol) (Found: C, 77·2; H, 5·7. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7%).

Further elution of the column with benzene gave a yellow uncrystallisable gum. It did not give a picrate and was not further examined. Final elution with ethanol then afforded a small amount of a red gum which solidified when kept. On crystallisation from benzene–light petroleum (b. p. 60—80°) a *methyl* ester (of X) separated as clusters of needles, m. p. 115° (Found: C, 72·9; H, 6·3. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%). Its 3:5-*dinitrobenzoate* formed small needles (from benzene–ethanol), m. p. 139° (Found: C, 61·7; H, 4·2; N, 5·5. $C_{26}H_{22}O_9N_2$ requires C, 61·7; H, 4·4; N, 5·5%). The *acid* (X) crystallised from benzene in prisms, m. p. 145—146° (Found: C, 72·4; H, 6·2. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%).

This acid (10 mg.) and sodium dichromate (30 mg.) in acetic acid (0·5 c.c.) were warmed at 60° for 5 hours. The resulting dark green solution was diluted with water (2 vols.) and set aside. β-9-Keto-1-fluorenylpropionic acid (7 mg.) separated in yellow rods. Crystallisation from dilute acetic acid gave crystals, m. p. and mixed m. p. 133—134°.

Cyclisation of β-9-Methoxy-1-phenanthrylpropionic Acid (II).—(*a*) A solution of the pure acid (1 g.) in anhydrous hydrogen fluoride was allowed to evaporate overnight. The product was extracted with sodium carbonate solution, and a washed and dried benzene solution of the residue was evaporated, yielding a yellow oil (0·8 g.) which solidified when rubbed with light petroleum (b. p. 60—80°). The yellow powder, containing some black gummy material, was crystallised from ethanol (charcoal) and then from benzene–light petroleum (b. p. 60—80°), giving 9-*methoxy*-7:8-*benzoperinaphthan*-1-*one* (VI) as clusters of yellow needles (0·5 g.), m. p. 130—131° (Found: C, 82·2; H, 5·4; OMe, 11·3. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3; OMe, 11·8%). Attempts to remove the yellow colour by extraction with concentrated hydrochloric acid or by chromatography on alumina were unsuccessful. The *semicarbazone* formed yellow blades, m. p. 225—226° (from benzene–ethanol) (Found: N, 13·0. $C_{19}H_{17}O_2N_3$ requires N, 13·2%).

(*b*) The acid (1 g.) and phosphorus pentachloride (0·85 g.) in pure benzene (10 c.c.) were kept at 0° for 2 hours, and then warmed gently on the water-bath for 5 minutes. A solution of stannic chloride (1·5 c.c.) in benzene (10 c.c.) was added to the cooled solution. Next morning the product was isolated, a neutral yellow gum (780 mg.) being obtained. This was extracted with boiling ethanol (10 c.c.), and the solution filtered. 9-Methoxy-7:8-benzoperinaphthan-1-one (0·6 g.) separated from the filtrate in yellow needles, m. p. 130—131° alone or mixed with the material obtained as above. The material insoluble in ethanol (23 mg.) was crystallised from benzene–ethanol, and gave soft needles of 10-*chloro*-3′-*keto*-9-*methoxy*-1:2-cyclo*penteno*-*phenanthrene* (VIII), m. p. 218—220° (Found: C, 72·6; H, 4·4. $C_{18}H_{13}O_2Cl$ requires C, 72·85; H, 4·4%).

Reduction of 9-*Methoxy*-7:8-*benzoperinaphthan*-1-*one* (VI).—The ketone (50 mg.) in ethanol (10 c.c.) was shaken in an atmosphere of hydrogen with platinum oxide catalyst (50 mg.). When one molecule of hydrogen had been absorbed, the filtered solution was evaporated, giving an oil from which 9-*methoxy*-7:8-*benzoperinaphthan*-1-*ol* was obtained as prisms (from ethanol), m. p. 181° (Found: C, 81·5; H, 5·8. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

The same carbinol was obtained when the ketone (20 mg.) in benzene (3 c.c.) was treated with a solution of lithium aluminium hydride (150 mg.) in ether (5 c.c.) for 12 hours at room temperature, and the mixture then heated under reflux for ½ hour. The carbinol crystallised from benzene–ethanol in prisms, m. p. and mixed m. p. 177—178°.

meso*Benzanthrone from* 9-*Methoxy*-7:8-*benzoperinaphthan*-1-*ol*.—Dry hydrogen chloride was passed for a few minutes into a solution of the perinaphthanol (30 mg.) in benzene (3 c.c.). After 12 hours the solution was washed with water and dried, and solvent removed under reduced pressure. The resulting yellow gum was chromatographed on alumina in benzene solution. A yellow band was eluted and the solution evaporated, yielding a gum from which a yellow solid (10 mg.) separated on trituration with ethanol. Crystallisation from ethanol gave deep

yellow prisms of *meso*benzanthrone, m. p. and mixed m. p. 166—168° (lit., 171°). The other bands of the chromatogram yielded small amounts of uncrystallisable oils which were not further examined.

Chlorination of β-9-*Methoxy*-1-*phenanthrylpropionic Acid.*—The acid (200 mg.) and phosphorus pentachloride (400 mg.) were heated on the water-bath for 15 minutes. The black mass was treated with ice and sodium carbonate solution, and the alkaline solution extracted with benzene and acidified. The product (171 mg.) was crystallised from acetic acid (charcoal) and then from benzene–light petroleum (b. p. 60—80°), forming fine, almost colourless needles of β-(10-*chloro*-9-*methoxy*-1-*phenanthryl*)*propionic acid*, m. p. 147—148° (Found : C, 68·7; H, 4·8. $C_{18}H_{15}O_3Cl$ requires C, 68·7; H, 4·8%).

10-*Chloro*-3′-*keto*-9-*methoxy*-1 : 2-cyclo*pentenophenanthrene* (VIII).—The above chloro-acid (22 mg.) and phosphorus pentachloride (20 mg.) in pure benzene (2 c.c.) were left for an hour at room temperature, and then warmed on the water-bath for a few minutes. The solution was cooled in ice, and stannic chloride (0·1 c.c.) in benzene (1 c.c.) added. After 12 hours the product (11 mg.) was isolated; it formed needles, m. p. 220° (from ethanol), identical with the ketone (VIII) obtained as already described.

1 : 2-cyclo*Penteno*-9 : 10-*phenanthraquinone from the Ketone* (VIII).—The chloro-ketone (37 mg.), amalgamated zinc (0·5 g.), concentrated hydrochloric acid (5 c.c.), acetic acid (1 c.c.), and toluene (1 c.c.) were boiled for 24 hours. Benzene was added and the organic layer separated, washed, dried, and evaporated. The resulting gum (33 mg.), after passage through a column of alumina, was treated with osmium tetroxide (33 mg.) in benzene (0·5 c.c.) containing a few drops of pyridine. After 5 days, *n*-hexane (1 c.c.) was added to the deep red solution, and the supernatant liquid poured off from the precipitated dark gummy complex. This was decomposed by refluxing it for 30 minutes with mannitol (200 mg.) and potassium hydroxide (20 mg.) in water (2 c.c.). The residual diol from two such treatments was oxidised with chromium trioxide (10 mg.) in acetic acid (2 c.c.). After 12 hours at room temperature the solution was heated to 60° for 30 minutes, diluted with water, and extracted with benzene. The washed and dried extract was concentrated and passed through a column of alumina. On development with benzene an orange band was formed. The solid (5 mg.) recovered from it crystallised from ethanol in deep orange needles, m. p. 209—211°, not depressed when mixed with an authentic specimen of 1 : 2-*cyclo*penteno-9 : 10-phenanthraquinone (IX). The identity of the specimens was confirmed by comparison of the azines, m. p. and mixed m. p. 194—196°.

Chromic Acid Oxidation of 1 : 2-cyclo*Pentenophenanthrene.*—A suspension of 1 : 2-*cyclo*pentenophenanthrene (8·75 g.) in acetic acid (100 c.c.) was treated dropwise, with water-cooling, with a solution of chromic acid (6·5 g.) in 80% acetic acid (15 c.c.). After 24 hours at room temperature the solid in suspension was collected, washed, and dried (*A*) (5 g.). The liquors were diluted with water and extracted with ether. The extract was washed with sodium carbonate solution, filtered from some suspended solid (*B*) (0·8 g.), and evaporated to dryness. The residue was warmed with a little alcohol, cooled, and filtered, yielding a solid (*C*) (1·7 g.).

Fraction *A* was crystallised from benzene, and the crystals (2·4 g.) further purified by high-vacuum sublimation at 140—160°. The sublimate was crystallised from acetone, yielding 1′-keto-1 : 2-*cyclo*pentenophenanthrene (XI) as needles, m. p. 185—186° (1·7 g.). A portion, crystallised from benzene, formed needles, m. p. 186—187°, not depressed when mixed with an authentic specimen, m. p. 183—184°, prepared by Bachmann and Kloetzel (*loc. cit.*) (Found : C, 87·8; H, 5·4. Calc. for $C_{17}H_{12}O$: C, 87·9; H 5·2%). This mixed m. p. determination was kindly carried out by the late Professor W. E. Bachmann. The *oxime* crystallised from benzene in needles, m. p. 238—240° (decomp.) (Found : C, 82·6; H, 5·4. $C_{17}H_{13}ON$ requires C, 82·5; H, 5·3%).

Fractions *B* and *C* were combined and treated with a solution of sodium hydrogen sulphite in aqueous ethanol. Acidification of the filtered solution with hydrochloric acid yielded 1 : 2-*cyclo*penteno-9 : 10-phenanthraquinone (IX), bright red needles (100 mg.) (from benzene), m. p. 209—211°, not depressed when mixed with an authentic specimen prepared as described by Butenandt, Dannenberg, and Dresler (*loc. cit.*), who give m. p. 213° (Found : C, 81·9; H, 4·7. Calc. for $C_{17}H_{12}O_2$: C, 82·2; H, 4·9%). Identity was confirmed by comparison of the *azines*, prepared from the quinone (0·1 g.) and *o*-phenylenediamine (0·1 g.) in acetic acid. The fine, pale yellow needles, obtained by crystallisation from *cyclo*hexane, had m. p. 194—196° (Found : C, 86·55; H, 4·9; N, 8·65. $C_{23}H_{16}N_2$ requires C, 86·2; H, 5·0; N, 8·75%).

Oxidation of 1 : 2-cyclo*Pentenophenanthrene with Lead Tetra-acetate.*—Freshly prepared lead tetra-acetate (3·1 g.) was added to a solution of 1 : 2-*cyclo*pentenophenanthrene (1·5 g.) in acetic acid (70 c.c.), and the whole heated on the water-bath for 30 minutes. The orange-

yellow solution was poured into water and extracted with benzene. The washed and dried extract was passed through a column of silica gel; on elution with benzene, strongly fluorescent material ran rapidly through the column. Evaporation of this eluate afforded unchanged 1 : 2-*cyclo*pentenophenanthrene, m. p. 133—135° (0·6 g.). Further elution with benzene then yielded a gum (0·95 g.) which afforded a colourless solid on trituration with light petroleum (b. p. 60—80°). After several crystallisations from ethanol, 1′-*acetoxy*-1 : 2-cyclo*pentenophenanthrene* (XII; R = COMe) was obtained as needles (250 mg.), m. p. 127—128° (Found : C, 83·0; H, 5·9. $C_{19}H_{16}O_2$ requires C, 82·8; H, 5·8%).

1′-*Hydroxy*-1 : 2-cyclo*pentenophenanthrene* (XII; R = H).—The above acetate (240 mg.) was hydrolysed by boiling its solution in ethanol (20 c.c.) with 40% potassium hydroxide (2 c.c.) for 1½ hours. 1′-*Hydroxy*-1 : 2-cyclo*pentenophenanthrene* (200 mg.) formed plates (from benzene), m. p. 166—167° (Found : C, 87·1; H, 6·2. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%).

This compound (10 mg.) was shaken at room temperature for 15 minutes with a solution of chromium trioxide (5 mg.) in 80% acetic acid (0·5 c.c.). Insoluble material was filtered off, washed, and crystallised from ethanol. 1′-Keto-1 : 2-*cyclo*pentenophenanthrene (XI) was obtained as pale yellow needles, m. p. and mixed m. p. 183—184°.

1 : 2-cyclo*Pentadienophenanthrene* (XIII).—The above carbinol (180 mg.), in pyridine (1·5 c.c.), was treated with benzoyl chloride (0·4 c.c.). After 18 hours at room temperature the solution was diluted with water, and the solid product recrystallised from benzene–light petroleum (b. p. 60—80°), furnishing the benzoate as needles, m. p. 176—177°. This product (150 mg.) was boiled with dimethylaniline (2 c.c.) for 8 hours, and the cooled solution poured into excess of hydrochloric acid. The washed and dried precipitate was sublimed at 140°/10^{-2} mm.; crystallisation of the sublimate from alcohol afforded 1 : 2-cyclo*pentadienophenanthrene* as leaflets (40 mg.), m. p. 163—164° (Found : C, 94·4; H, 5·6. $C_{17}H_{12}$ requires C, 94·4; H, 5·6%). The *s*-trinitrobenzene *complex* formed canary-yellow needles, m. p. 172—173° (from ethanol) (Found : C, 64·6; H, 3·5. $C_{17}H_{12},C_6H_3O_6N_3$ requires C, 64·3; H, 3·5%). The picrate crystallised from ethanol in fine orange-red needles, m. p. 146—147°.

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