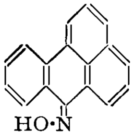
153. *Reactivity of the Carbonyl Group in* meso*Benzanthrone.*

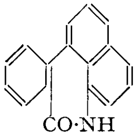
By Neil Campbell and A. A. Woodham.

*meso*Benzanthrone slowly forms an oxime which undergoes the Beckmann transformation to give a lactam whose structure has been established by synthesis and oxidation. Reduction with the Meerwein–Ponndorf reagent unexpectedly gives *meso*benzanthrene and provides the best method for the synthesis of this hydrocarbon. *meso*Benzanthrone with phosphorus pentachloride and phosphorus oxychloride gives dinuclear products, and with certain acids forms oxonium salts which have been examined by Kofler's "contact method."

Although *meso*benzanthrone undoubtedly contains a carbonyl group, no effort has been made, so far as we are aware, to prepare the oxime, etc. We have, therefore, studied the oximation of *meso*benzanthrone and found that the carbonyl group reacted very sluggishly. Heating *meso*benzanthrone with hydroxylamine hydrochloride in pyridine for 8 hours gave little or no oxime, but extending the period to 20 and 70 hours gave yields of 30—50% and 80% respectively of an oxime (I). The oxime of 3-chloro*meso*benzanthrone was prepared similarly.



(I)



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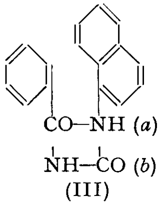

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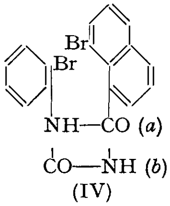


(IV)

The oxime (I) underwent the Beckmann rearrangement when treated with phosphorus pentachloride and phosphorus oxychloride (cf. Moore and Huntress, *J. Amer. Chem. Soc.*, 1927, **49**, 2621) to give a lactam (II) and a chloro-derivative which must be the chloro-derivative of either (I) or (II) (cf. Moore and Huntress, *loc. cit.*). The lactam is completely resistant to hydrolysis and thereby resembles the analogous phenanthridone.

Efforts were made to synthesise the lactam, or its isomer in which the NH and CO groups are interchanged, by the pyrolytic ring closure of *N*-benzoyl-α-naphthylamine (III*a*) and of 1-naphthanilide (III*b*) (cf. Meyer and Hofmann, *Monatsh.*, 1916, **37**, 681). The former gave a small quantity of a substance which is certainly not a *meso*benzanthrone lactam, and the latter yielded only naphthalene and unchanged material. The method was, therefore, abandoned in favour of the intramolecular condensations of the *o*-bromoanilide (IV*a*) of 8-bromo-1-naphthoic acid and 8-bromo-*N*-*o*-bromobenzoyl-1-naphthylamine (IV*b*). The first compound gave three products: *N*-phenylnaphthastyril, formed by the interaction of the naphthalene-bromine atom with the amino-group and subsequent dehalogenation; a substance of low m. p., high solubility in organic solvents, and blue fluorescence in solution; and a minute quantity of what may be a lactam. The second, however, gave a small quantity of a product identical with the lactam obtained from the Beckmann transformation. The lactam must therefore have the structure (II), and this was confirmed by its oxidation with alkaline permanganate to phthalic acid in almost quantitative yield: no naphthalic acid could be detected. From the structure of the lactam (II) it follows that the oxime is (I).

Under drastic conditions *meso*benzanthrone formed a 2 : 4-dinitrophenylhydrazone in poor yield.

Attempts were made to see if the carbonyl group of *meso*benzanthrone is reduced to the CH·OH group by aluminium *iso*propoxide. Reduction was readily effected, but surprisingly resulted in the complete removal of oxygen to give a good yield of *meso*benzanthrene. A good method is thereby provided for the preparation of *meso*benzanthrene and certain substituted *meso*benzanthrenes. The method was successfully applied to the preparation of 3-chloro- and 3-bromo-*meso*benzanthrene, but 11-amino*meso*benzanthrone gave only unchanged material, probably owing to its insolubility in *iso*propanol; and 4-benzyl*meso*benzanthrone gave a small yield of what seemed to be the carbinol. So far as we are aware the one other example of the reduction of a carbonyl to a methylene group by the Meerwein–Ponndorf reagent is the slow conversion of 9 : 9-dimethylanthrone into the dihydroanthracene (Adkins and Rossow, "Organic Reactions," Vol. II, p. 191). The only other comparable reaction which comes to mind is the reduction of xanthone to xanthen by sodium and ethanol (Heller and von Kostanecki, *Ber.*, 1908, **41**, 1324; Kruber and Lauenstein, *ibid.*, 1941, **74**, 1693). We have reduced anthrone by aluminium *iso*propoxide and found that it gives anthracene. Presumably 9 : 10-dihydroanthranol is first formed and loses water to give anthracene (cf. Houben, "Das Anthracen und die Anthrachinone," p. 167, G. Thieme, Verlag, Leipzig).

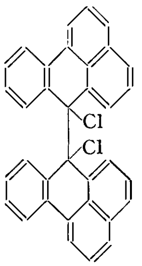
The basic properties of the carbonyl group in *meso*benzanthrone are reflected in the formation of oxonium salts. Perkin (*J.*, 1920, 696), from the colour of the solution, surmised that *meso*benzanthrone forms an oxonium salt with concentrated sulphuric acid. By the Kofler method (Kofler and Kofler, "Mikromethoden zur Kennzeichnung organischen Stoffe und Stoffgemische," Universitätsverlag, Innsbruck, 1948) we have shown that an oxonium salt, m. p. 184°, is indeed formed. Trichloroacetic acid also gives an oxonium salt, but the weaker chloroacetic, benzoic, and adipic acids give only eutectic mixtures. Fluorenone and phenanthraquinone likewise form oxonium salts with trichloroacetic acid, that of the former compound having m. p. 37° which differs from the 58° assigned by Meyer (*Ber.*, 1910, **43**, 162). We repeated the preparation by Meyer's method and obtained yellow plates, m. p. 37°, thereby confirming the m. p. obtained by the micro-method. The pronounced tendency of *meso*benzanthrone and fluorenone to form oxonium salts is emphasised by the failure of benzylideneacetophenone to form an oxonium salt with trichloroacetic acid, in spite of the known fact that αβ-unsaturated ketones are particularly prone to oxonium compound formation (see, *e.g.*, Wheland, "Advanced Organic Chemistry," p. 41).

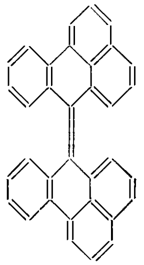
*meso*Benzanthrone and fluorenone form molecular compounds with picric acid and 1 : 3 : 5-trinitrobenzene. The isolation of these compounds is not easy, but their formation is conclusively shown by the Kofler "contact process."

We subjected *meso*benzanthrone to the action of hydrazoic acid under a variety of conditions, but obtained only unchanged ketone.

*meso*Benzanthrone when heated with phosphorus pentachloride and oxychloride gave two products, both of which dissolve in benzene, ethanol, etc., to give yellow solutions with a vivid green fluorescence. One of these substances was obtained as orange needles, m. p. 390°, and contained chlorine. The mode of formation, analytical results, and molecular weight of approximately 500 suggest that this substance is 7 : 7′-dichloro-7 : 7′-di*meso*benzanthrenyl (V). Treatment of *meso*benzanthrone with phosphorus oxychloride alone yielded a product which crystallised in yellow needles, m. p. 346—347°, which proved to be identical with the hydrocarbon obtained as one of the products when *meso*benzanthrone is distilled over zinc dust (Zinke *et al.*, *Monatsh.*, 1950, **81**, 878, 1137). We are indebted to Professor A. Zinke, of the University of Graz, for supplying us with a specimen. Our analytical figures indicate that the hydrocarbon is 7 : 7′-di*meso*benzanthrylidene (VI) which differs from the structure tentatively suggested by Zinke *el al.* (*loc. cit.*). Further work however is required before a structure can be assigned with finality.

(V)





(VI)

EXPERIMENTAL

All chromatographic separations were effected on alumina (B.D.H. chromatographic), and the thermal behaviour of substances was examined on the Kofler hot-stage microscope (*Mikrochem.*, 1934, **15**, 242).

meso*Benzanthrone Oxime.*—Purified *meso*benzanthrone (10 g.), hydroxylamine hydrochloride (50 g.), and pyridine (250 ml.) were gently boiled for 70 hours. Most of the pyridine was then distilled off and the residue poured into water (150 ml.). Extraction with ether, followed by evaporation of the ethereal layer to a small volume and addition of the same volume of ethanol, gave a 85—95% yield of crude oxime, m. p. 160—165°. The oxime in benzene was passed down a column (18 × 1″) and on development with benzene *meso*benzanthrone passed rapidly through leaving the oxime at the top of the column as a dull yellow zone with a faint yellow fluorescence. Extraction of this zone with ethanol gave meso*benzanthrone oxime*, pale yellow rhombohedral plates (from methanol), m. p. 171° (6·8 g., 65%) (Found : C, 82·8; H, 4·5; N, 5·5. $C_{17}H_{11}ON$ requires C, 83·3; H, 4·5; N, 5·7%). The oxime is readily hydrolysed to *meso*benzanthrone by boiling ethanolic sulphuric acid, and even crystallisation from glacial acetic acid causes partial hydrolysis.

3-*Chloro*meso*benzanthrone oxime* (35%) was similarly prepared, and separated from methanol in pale orange prisms, m. p. 205° (Found : N, 5·2; Cl, 13·3. $C_{17}H_{10}ONCl$ requires N, 5·0; Cl, 12·7%).

Beckmann Rearrangement of meso*Benzanthrone Oxime.*—*meso*Benzanthrone oxime (3·0 g.), phosphorus pentachloride (3·8 g.), and phosphorus oxychloride (50 ml.) were gently boiled for 1½ hours, and the oxychloride removed by distillation. The residue was stirred with a little water and repeatedly extracted with benzene. The combined benzene extracts (600 ml.), when kept overnight, deposited a *chloro*-compound, which crystallised from ethanol in colourless needles, m. p. 288° (0·17 g.) (Found : N, 4·9; Cl, 13·1. $C_{17}H_{10}NCl$ requires N, 5·3; Cl, 13·4%). The filtrate was passed down a column (12 × 1″), and development with benzene gave a yellow zone of *meso*benzanthrone (0·24 g.) which quickly passed down the column. Continued development gave at the bottom a buff-coloured zone which on extraction with ethanol afforded the *lactam* (II), m. p. 234°, of 8-*o*-carboxyphenyl-1-naphthylamine (Found : C, 82·9; H, 4·6; N, 5·7. $C_{17}H_{11}ON$ requires C, 83·3; H, 4·5; N, 5·7%).

Structure of the Lactam (II).—The lactam (0·5 g.) in concentrated sulphuric acid (4 ml.) was added with stirring to water (50 ml.). The suspension was made alkaline with 6N-sodium hydroxide, and water was added to make the volume up to 125 ml. Potassium permanganate (3 g.) was added and the mixture refluxed for 17 hours. The product was proved to be phthalic acid by m. p. (205—210° on rapid heating), mixed m. p., fluorescein test, and preparation of the aniline salt, m. p. 154°. The complete absence of naphthalic acid was shown by the failure of the product to give a colour with concentrated sulphuric acid.

8-Bromo-1-naphthoic acid (12 g.) was converted by sodium azide (5 g.) and concentrated sulphuric acid (100 ml.) into 8-bromo-1-naphthylamine (10·6 g.), m. p. 82—86°, which with *o*-bromobenzoyl chloride afforded *8-bromo-*N-o-*bromobenzoyl-1-naphthylamine*, elongated prisms (from methanol), m. p. 142° (Found: N, 3·3; Br, 38·9. $C_{17}H_{11}ONBr_2$ requires N, 3·5; Br, 39·5%). This substance (1·8 g.) and copper bronze (1·6 g.) were heated at 250—260° for 2 hours. The mixture was extracted with acetone and on evaporation gave a residue which was dissolved in benzene and chromatographed. Development with benzene gave a number of zones one of which occupied the same place on the column as that from the Ullmann product described below which yielded high-melting material. Extraction of this band with ethanol yielded 10 mg. of a substance, m. p. 224—230°, which when mixed with the Beckmann rearrangement product (m. p. 234°) melted at 226—228°. Both substances dissolved in sulphuric acid to give yellow solutions with a faint yellow fluorescence.

Ring-closure of 8-*Bromo*-1-*naphthoic Acid* o-*Bromoanilide*.—The acid chloride from 8-bromo-1-naphthoic acid (5 g.) and *o*-bromoaniline (8 g.) in benzene gave the o-*bromoanilide*, needles (from aqueous methanol), m. p. 145—146° (7·2 g.) (Found: N, 3·4; Br, 39·5. $C_{17}H_{11}ONBr_2$ requires N, 3·5; Br, 39·5%). The bromoanilide (2·0 g.) and copper bronze (1·8 g.) were stirred at 255—260° for 2 hours and worked up as above. Development of the column with benzene gave a zone with a strong blue fluorescence even in daylight. Elution of this zone and concentration of the eluate gave a *substance*, prisms [from light petroleum (b. p. 60—80°)], m. p. 102° (Found: C, 82·5; H, 4·6; N, 5·5. $C_{17}H_{11}ON$ requires C, 83·3; H, 4·5; N, 5·7%). On the column a large yellow zone with a yellow fluorescence remained which yielded *N*-phenylnaphthastyril, pale yellow needles (from light petroleum), m. p. 106° (Found: C, 83·1; H, 4·6; N, 5·7. Calc. for $C_{17}H_{11}ON$: C, 83·3; H, 4·5; N, 5·7%). There remained at the top of the column, directly below a black region of impurity, a fawn-coloured, non-fluorescent zone which was separated and extracted with methanol. Concentration of the extract gave a little material which, crystallised from methanol, had m. p. 240—250°. It contained no halogen and showed a big m. p. depression when admixed with the lactam (II). It is possible that this substance is the isomeric lactam.

Reduction of meso*Benzanthrone, etc.*—*meso*Benzanthrone (0·5 g.), *iso*propanol (20 ml.), and aluminium *iso*propoxide solution (10 ml.) (from 100 ml. of *iso*propanol and 5 g. of aluminium) were refluxed for 20 hours. The flask was then fitted with a Hahn condenser containing methanol, and slow distillation was carried out until all the acetone was removed and the volume was reduced to approx. 10 ml. A further quantity of *iso*propoxide solution (5 ml.) and *iso*propanol (20 ml.) was added and the solution boiled for 20 hours. The acetone was then distilled off and the solution concentrated to about 10 ml. The residue was treated with dilute sulphuric acid and extracted with boiling benzene. The extract was then chromatographed. Development with benzene gave a colourless zone showing strong violet fluorescence, which passed rapidly down the column to yield a colourless solid (0·37 g.), m. p. 75—77°, which crystallised from ethanol in almost colourless plates of *meso*benzanthrene, m. p. 80—82° (Found: C, 94·3; H, 5·3. Calc. for $C_{17}H_{12}$: C, 94·4; H, 5·6%). The product gave a picrate, red needles, m. p. 110—111° (lit., 110—111°), and dissolved in concentrated sulphuric acid with a faint red fluorescence.

Pure 3-chloro*meso*benzanthrone (1 g.), aluminium *iso*propoxide solution (15 ml.), and *iso*propanol (30 ml.) were gently boiled for 18 hours. Alternate distillation and refluxing were then carried out until no acetone was produced after 1 hour's refluxing. The product was worked up as above and chromatographed on a column (18″ × ¾″). Development with light petroleum–benzene (4 : 1) gave a blue fluorescent zone which passed quickly down the column and yielded 3-*chloro*meso*benzanthrene* (0·63 g.), rosettes (from light petroleum), m. p. 110° (Found: C, 81·2; H, 4·4; Cl, 13·8. $C_{17}H_{11}Cl$ requires C, 81·4; H, 4·4; Cl, 14·2%). 3-Bromo*meso*benzanthrone similarly gave 3-*bromo*meso*benzanthrene* (70%), needles (from light petroleum), m. p. 116° (Found: C, 69·2; H, 3·7; Br, 26·4. $C_{17}H_{11}Br$ requires C, 69·1; H, 3·7; Br, 27·1%).

4-Benzyl*meso*benzanthrone (0·5 g.), aluminium *iso*propoxide solution (15 ml.), *iso*propanol (20 ml.), and benzene (100 ml.) were boiled for 25 hours; and then alternately distilled and refluxed for a further 5 hours. Working up the solution as above and chromatographing on a column (12 × 1″) gave a zone with a violet fluorescence typical of *meso*benzanthrenes, from which, however, only a trace of solid was obtained. A yellow zone which followed was washed through and deposited yellow prisms of what may be the 4-*benzyl*meso*benzanthrol* (20 mg.), m. p. 127—128° (Found: C, 90·8; H, 6·0. $C_{24}H_{18}O$ requires C, 89·5; H, 5·6%). An upper yellow layer on the column afforded unchanged benzyl*meso*benzanthrone (0·2 g.).

Anthrone (0·5 g.), aluminium *iso*propoxide solution (10 ml.), and *iso*propanol (20 ml.) were boiled for 40 hours and then slowly distilled. A practically quantitative yield of anthracene was obtained.

Oxonium Salts of meso*Benzanthrones.*—The formation of oxonium salts was established by the microscopic technique of Kofler and Kofler (*op. cit.*). By this technique the melting-points of the components and of the molecular compound (*e.g.*, oxonium salts), and the eutectic points of the molecular compound and the two components are determined. The results are tabulated below.

Component A	Component B	M. p. of molecular compound (M)	Eutectic A–M	Eutectic B–M
*meso*Benzanthrone	Picric acid	142°	138°	115°
,,	Trinitrobenzene	140	138	116
,,	$CCl_3{\cdot}CO_2H$	95	88	47
,,	H_2SO_4	184	140	—
Fluorenone	Picric acid	95	72	94
,,	Trinitrobenzene	80	72	75
,,	$CCl_3{\cdot}CO_2H$	37	24	22
Phenanthraquinone	,,	138	133	39

The following pairs of substances formed only eutectics (m. p. in parentheses) : *meso*benzanthrone–chloroacetic acid (53°), *meso*benzanthrone–adipic acid (148°), *meso*benzanthrone–benzoic acid (109°), benzylideneacetophenone–picric acid (49°), benzylideneacetophenone–trichloroacetic acid (53°).

Action of Phosphorus Pentachloride and Oxychloride on meso*Benzanthrone.*—*meso*Benzanthrone (0·5 g.) was boiled for 5 hours in phosphorus oxychloride (10 ml.) and phosphorus pentachloride (0·65 g.). The oxychloride was then distilled off, the residue triturated with water, and the resulting dark solid extracted with boiling benzene. Concentration of the extract, followed by chromatography on a column (8 × 1″), gave a yellow zone which moved rapidly down the column to give a yellow solution with a vivid green fluorescence. Concentration of this solution to about 10 ml. afforded orange needles of 7 : 7′-*dichloro*-7 : 7′-*di*meso*benzanthrenyl* (0·2 g.), m. p. 390° (Found : C, 81·8; H, 3·4; Cl, 14·1. $C_{34}H_{20}Cl_2$ requires C, 81·8; H, 4·0; Cl, 14·2%). From the column a red solid, m. p. 320°, was isolated but was not further investigated.

*meso*Benzanthrone (0·5 g.) and phosphorus oxychloride (10 ml.) were boiled for 1½ hours. The oxychloride was distilled off, and the residue triturated with water. Extraction of the residue with benzene (1—1½ l.) dissolved only a portion of the solid. The solution was concentrated to 100 ml. and then passed down a column (30″ × 1″). Development with benzene–light petroleum (b. p. 60—80°) (4 : 1) gave a greenish-yellow zone with a bluish-green fluorescence which was the first to be washed through. The solution, which exhibited a striking bluish-green fluorescence even in daylight, gave on concentration 7 : 7′-*di*meso*benzanthrylidene* (?), yellow needles (from benzene), m. p. 346—347° (Found : C, 95·0; H, 4·6. $C_{34}H_{20}$ requires C, 95·3; H, 4·7%).

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