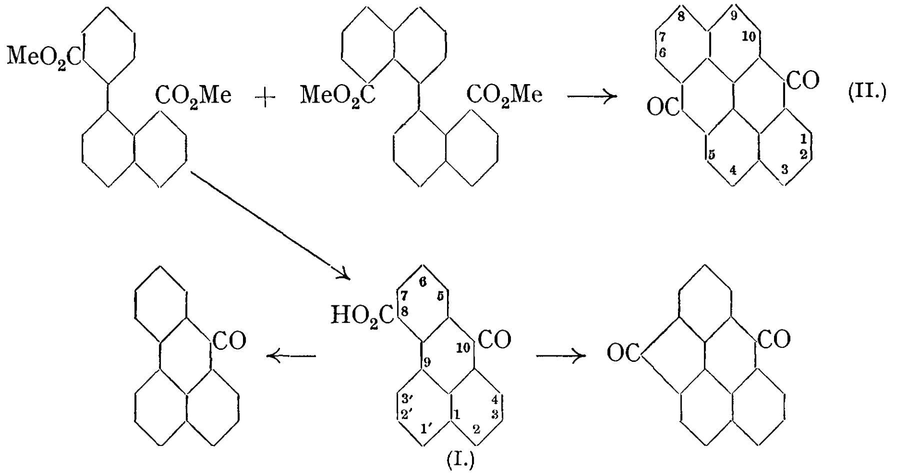
230. *Synthesis of* meso*Benzanthrones and Anthanthrones by the Ullmann Method.*

By H. GORDON RULE and F. RANDALL SMITH.

THE discovery that 8-bromo-1-naphthoic acid may be prepared readily from naphthalic acid (Rule and co-workers, J., 1934, 170) opens the way to the synthesis by Ullmann's reaction not only of substituted anthanthrones, but also of *meso*benzanthrones in cases where it is possible to obtain the unsymmetrical phenyl-naphthyl intermediates required for conversion into the latter group by cyclisation. Unfortunately the production of unsymmetrical dinuclear compounds by Ullmann's method cannot always be effected in good yield. Provided that the two halogen derivatives R_1X and R_2X are equally reactive towards copper bronze, an equimolecular mixture of them may be expected to give approximately equal proportions of the three products R_1R_1, R_2R_2, and R_1R_2. Apparently these conditions hold in the case of the *o*- and *m*-iodotoluenes, from a mixture of which the unsymmetrical 2 : 3-ditolyl has been isolated in a yield of 27—30% (Mayer and Freitag, *Ber.*, 1921, **54**, 356). But the halogen in one of the components may be rendered relatively inert through steric hindrance due to an adjacent group or alternatively become abnormally active owing to the presence of certain substituents in the molecule, with the result that the yield of the unsymmetrical dinuclear product is frequently diminished almost to vanishing point. In some cases, however, reactions of this type have been carried out successfully, as is illustrated by the coupling of iodobenzene and iodonaphthalene, respectively, with 2-chloro-3 : 5-dinitrobenzoic ester (Lesslie and Turner, J., 1930, 1758; 1931, 1188), from which the unsymmetrical derivatives were isolated in about 54% yields, no other products being detected.

The present communication deals with the reaction between 8-bromo-1-naphthoic ester and *o*-iodobenzoic ester, more particularly with the optimum conditions required for the formation of the unsymmetrical phenyl-naphthyl dicarboxylate and the influence exerted upon the course of the reaction by the introduction of substituents into the benzene and naphthalene nuclei. From the products so obtained, a number of derivatives of benzanthrone and anthanthrone have been isolated. Rule, Pursell, and Barnett carried out this reaction at 215—220°, using the iodobenzoic ester in 50% excess, and obtained pure crystalline methyl 8-*o*-carbomethoxyphenyl-1-naphthoate in a yield of 40% (J., 1935, 571).

In the experiments now described, the resulting reaction mixture of phenyl-naphthyl, dinaphthyl, and diphenyl derivatives was heated with sulphuric acid and the yields of the individual products were estimated from the amounts of 8-carboxy*meso*benzanthrone (I) and anthanthrone (II) obtained. Since the reaction with copper bronze was carried to completion, any iodobenzoate remaining unaccounted for was assumed to have been converted into diphenyldicarboxylic acid. All yields recorded below are calculated on the amount of bromonaphthoate employed, and on this basis the maximum yield of unsymmetrical derivative (75%) was obtained by use of two molecular proportions of iodobenzoate and a temperature of 180°; 11% of anthanthrone was also isolated, these two compounds corresponding to 86% of the original bromonaphthoate. Subsequently, experiments were carried out in which substituents were present in one or both of the reacting molecules, and, as the material was insufficient for repeated preparations, the above conditions for the Ullmann reaction were adopted in each case. In general, 80—90% of the naphthoate could be accounted for in this way. A summary of the more definite results is given in the table, two molecular proportions of the benzoic ester being used to one of the naphthoate except in No. 1, in which equal proportions were employed. The yields recorded could be repeated without difficulty.



(II.)

(I.)

Ullmann Reactions.

	Temp.	% Benzanthrone.	% Anthanthrone.
Methyl 8-*bromo*-1-*naphthoate in reaction with :*			
(1) Methyl *o*-iodobenzoate (1 mol. only)	195°	54	31
(2) Methyl *o*-iodobenzoate (2 mols.)	180	75	11
(3) Methyl *o*-bromobenzoate	180	41	44
(4) Methyl *o*-chlorobenzoate	180	—	71
(5) Methyl 5-bromo-2-iodobenzoate	180	60	28
(6) ,, ,, ,,	220	27	53
(7) Methyl 2-iodo-5-nitrobenzoate	180	41	43
(8) Methyl 2-bromo-5-nitrobenzoate	180	33	60
Methyl o-*iodobenzoate in reaction with :*			
(9) Methyl 5 : 8-dibromo-1-naphthoate	180	49	32
(10) Methyl 8-bromo-5-nitro-1-naphthoate	180	49	35
Methyl 5 : 8-*dibromo*-1-*naphthoate in reaction with :*			
(11) Methyl 5-bromo-2-iodobenzoate	180	49	38
(12) ,, ,, ,,	220	36	41
Methyl 8-*bromo*-5-*nitro*-1-*naphthoate in reaction with :*			
(13) Methyl 2-iodo-5-nitrobenzoate	180	—	75

As has already been stated, the experimental conditions adopted in No. 2 lead to a maximum yield of the unsymmetrical product, hence it is to be anticipated that smaller yields will result if the reactivity of either component is modified with respect to the other. Thus the activity of halogen in the iodobenzoate may be diminished by replacing iodine with bromine or chlorine (Nos. 3 and 4), or enhanced by introducing a nitro-group into the para-position to iodine (No. 7). Similarly, bromine in the bromonaphthoate may be further activated by the presence of a nitro-group * in position 5 (No. 10). In all of these cases the changes resulted in lower yields of the phenyl-naphthyl derivative.

Among other variations, reference may be made to No. 11, in which the modification of both reacting components by the introduction of bromine into the para-position to each halogen atom led to a reduction in the yield of phenyl-naphthyl derivative from 75% to 49%, and the corresponding introduction of *p*-nitro-groups (No. 13) resulted unexpectedly

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* The activating influence of the 5-nitro-group has been proved in the reactivity of the bromine atom towards sodium methoxide (W. S. Haldane, Thesis, Edinburgh, 1934) : but the effect of a 5-bromo-substituent (No. 9) in the above series is unexpectedly marked.

in the almost complete disappearance of the unsymmetrical product and a very high yield of anthanthrone.

In two instances (Nos. 6 and 12) the Ullmann reaction was carried out at 220° instead of 180°, in each case leading to an increase in the yield of anthanthrone at the expense of benzanthrone. Several other reactions in which difficulty was experienced in purifying the products or in effecting a conversion into benzanthrone are dealt with in the experimental section.

Three of the cases discussed above involve dihalogenated derivatives, but under the experimental conditions adopted there was no evidence of appreciable reactivity of halogen unless in the ortho- or peri-position to a carboxyl group. When 2 : 4-dibromobenzoic ester was employed as the benzenoid component, however, an inseparable mixture of derivatives produced by the coupling of both halogens was formed.

On the whole the effects of substitution support the view that the yield of unsymmetrical product is governed in part by the relative reactivities of the halogen atoms. Steric hindrance of the more active halogen is probably another controlling factor, visible in the interaction between picryl chloride and iodobenzene (Gull and Turner, J., 1929, 491), which leads only to the isolation of 2 : 4 : 6-trinitrodiphenyl. According to Ullmann (*Annalen*, 1904, **332**, 38) iodobenzene does not react with copper bronze below 220°. This point has been confirmed during the present investigation, and it has been found, in addition, that no appreciable reaction occurs when the iodobenzene is in solution in boiling nitrobenzene at 205°. Picryl chloride, on the other hand, is so reactive that the mixture with copper bronze explodes at about 135° ; although in boiling nitrobenzene the reaction proceeds smoothly to form hexanitrodiphenyl (Ullmann, *loc. cit.*). Gull and Turner used equimolecular quantities of reactants at 200—205° with gradual addition of copper bronze. No actual yield is recorded by these authors and it was considered of interest to repeat this work. At 195—203° the sole detectable product was trinitrodiphenyl, isolated in a yield of 75%. As it was not improbable that the temperature during this experiment might have risen locally to a point at which iodobenzene would normally be reactive, the change was carried out at 160—165° ; the yield of 2 : 4 : 6-trinitrodiphenyl then increased to 85%. These results suggest that in the presence of picryl chloride the relatively non-reactive iodobenzene undergoes some special form of activation, permitting it to enter into reaction at a temperature much below that at which it would ordinarily do so.

meso*Benzanthrones*.—Ring closure of all of the phenyl-naphthyl dicarboxylic esters mentioned in the table to benzanthrone and hydrolysis of the remaining carboxylic ester group were complete after treatment with concentrated sulphuric acid for one hour at 100°. The substituted *meso*benzanthrone-8-carboxylic acids so prepared, *viz.*, the 1'-*bromo*-, 6-*bromo*-, 1' : 6-*dibromo*-, 1'-*nitro*-, and 6-*nitro*-derivatives, were yellow crystalline compounds which dissolved in sulphuric acid with a blood-red colour. The bromo-acids were soluble in alkali, forming orange to red solutions having a strong green fluorescence ; the nitro-acids gave red non-fluorescent solutions.

When these acids were decarboxylated in boiling quinoline with addition of copper bronze, they gave rise to the corresponding substituted benzanthrones. 1'-Bromobenzanthrone melted at 176—177° and was identical with the product obtained by direct bromination of benzanthrone in acetic acid solution or in aqueous suspension. This synthesis therefore removes any remaining doubt that halogenation occurs primarily in the 1'-position. Further bromination is stated to yield a homogeneous product (Badische Anilin und Soda Fabrik, 1908, D.R.-P. 193,959), m. p. 256°, which must be designated as 1' : 6-*dibromo*-meso*benzanthrone*, since the compound obtained by brominating 1'-bromobenzanthrone in aqueous suspension is now found to be identical with that formed by decarboxylation of 1' : 6-dibromobenzanthrone-8-carboxylic acid. 6-Bromobenzanthrone, prepared by decarboxylation of the related acid, had a melting point of 183°, in agreement with that recorded for the product obtained by reducing 2 : 6-dibromobenzanthrone in alkaline medium (I.G., 1927 ; D.R.-P. 450,445).

The nitration of *meso*benzanthrone in nitrobenzene solution at 40—50° yields a mononitro-compound, m. p. 248—249°, in which the substituent occupies the 1'-position (B.P. 291,131, 1927) ; but in boiling acetic acid solution the main product is the isomeric 2'-nitrobenzanthrone, m. p. 305—307° (Meister, Lucius, and Bruning, 1923, B.P. 224,522). In the present investigation 1′-nitrobenzanthrone prepared from the corresponding carboxylic acid melted at 248—249°, and was identified with the compound obtained by nitrating benzanthrone in nitrobenzene solution. Synthetic *6-nitro*meso*benzanthrone* melted at 291—292°, and its melting point was strongly depressed by the second nitration product, m. p. 305—307°, obtained from benzanthrone in acetic acid solution.

Whereas the mononitro-derivatives obtained by direct nitration give orange non-fluorescent solutions in concentrated sulphuric acid, 6-nitrobenzanthrone forms a yellow solution with bright green fluorescence. 1′ : 6-Dinitrobenzanthrone is also stated to give a similar fluorescence, which thus appears to be characteristic of the nitro-group in position 6. It was not found possible to effect the synthesis of the 1′ : 6-dinitrobenzanthrone by the Ullmann method, or of the 5- or 7-nitro-compound.

In general, the oxidation of the substituted benzanthrones was not investigated, but 1′-bromobenzanthrone-8-carboxylic acid on treatment with chromic oxide was converted into the lactone of *1′-bromo-3′-hydroxybenzanthrone-8-carboxylic acid* (cf. Grieve and Rule, this vol., p. 535).

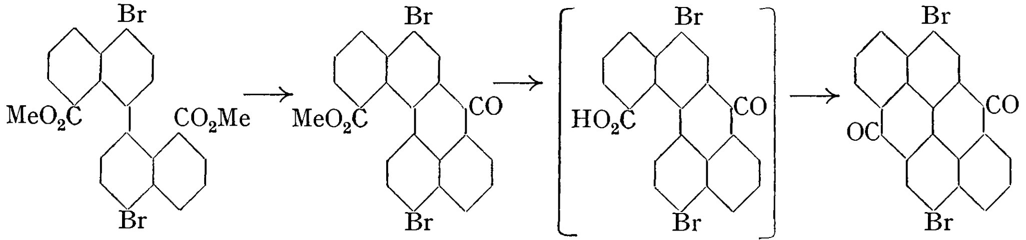
3′ : 8-*Keto*meso*benzanthrones.*—Further ring closure between the 8-carboxyl group and the hydrogen atom in position 3′ was brought about in a number of cases by heating the acid with phthalic anhydride and phosphoric oxide at 200° (cf. Bigelow and Rule, J., 1935, 573), thus leading to the related 3′ : 8-keto*meso*benzanthrones in little short of quantitative yield. The *6-bromo-*, *1′-bromo-*, *1′ : 6-dibromo-*, *6-nitro-*, and *1′-nitro-3′ : 8-keto*meso*benzanthrones* so obtained were crystalline compounds, ranging from orange to red, the 1′-nitro-derivative having the lightest colour and the dibromo-compound the deepest. In sulphuric acid they dissolve to give purple solutions. The melting points of these compounds and of the corresponding benzanthrones and their carboxylic acids show a curious irregularity. Whereas substitution by bromine or a nitro-group raises the melting point of benzanthrone or of its 8-carboxylic acid, that of the 3′ : 8-keto-compound is lowered. This is particularly marked in the case of the 6-bromo-ketone, which melts 88° lower than unsubstituted ketobenzanthrone.

A characteristic property of the 1′-bromo-ketone is the sintering observed at a well-marked temperature varying between 180° and 200°, with no further change until the melting point at 326—328°. This sintering may be eliminated by previously raising the compound above its fusion point, but reappears if the compound is again recrystallised or thrown out of a sulphuric acid solution by addition of water.

Benzanthrones and ketobenzanthrones in general do not possess the properties of vat dyes, but no reference appears to be made in the literature to the fact that 1′-nitrobenzanthrone is readily reduced by alkaline hyposulphite (hydrosulphite) to a deep blue vat which deposits the pink amino-compound on aerial oxidation. *Methyl 1′ : 6-dibromo-7 : 8-benzo*meso*benzanthrone-4″-carboxylate* (IV) also vats comparatively readily, giving a purple solution which deposits an orange ester on oxidation. Probably the reduction products in these cases are of the dihydrobenzanthrone type and not true leuco-compounds (cf. Bally and Scholl, *Ber.*, 1907, **40**, 1661).

Anthanthrones.—In the ring closure of 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic ester with warm sulphuric acid it has been assumed by Kalb (*Ber.*, 1914, **47**, 1724) that the red intermediate stage corresponds to the existence of the half cyclised product, benzo*meso*benzanthronecarboxylic acid, which eventually undergoes further ring closure to form the green solution of anthanthrone. During the present work, however, it was found that, if the red solution obtained by heating methyl 4 : 4′-dibromo-1 : 1′-dinaphthyl-8 : 8′-dicarboxylate (III) with sulphuric acid for 10 minutes at 50° were poured into water, the ester (IV) was deposited in 50% yield, admixed with unchanged material. No free acid (V) or anthanthrone (VI) was detected. A similar result was obtained with the unbrominated ester, indicating that the monocarboxylic ester of type (IV) is relatively stable under experimental conditions which rapidly transform the free acid into anthanthrone. A comparison (carried out with the aid of Mr. J. S. Flanders) has shown that benzo*meso*benzanthrone-carboxylic acid is converted by cold sulphuric acid into anthanthrone in two or three minutes, whereas the corresponding ester requires three days to effect the same change.

This stability is undoubtedly due to the increased steric hindrance offered to further hydrolysis after one carboxyl group has undergone ring closure, and thus brought the remaining ester complex into the same plane as the benzanthrone molecule, in spatial proximity to the 3′-position. In the related free acid, however, the carboxyl group is held rigidly in the position most favourable for rapid conversion of the compound into anthanthrone. It must therefore be concluded that the assumption made by Kalb (*loc. cit.*) is incorrect, and that the intermediate present in the red solution obtained by treating the dinaphthyldicarboxylic ester with sulphuric acid is predominantly benzo*meso*benzanthronecarboxylic ester and not the acid to which it gives rise on hydrolysis. The above dibromodinaphthyldicarboxylic ester passed into the anthanthrone much more slowly than the unsubstituted compound, requiring at least ten times as long at 50° to yield a pure green solution in sulphuric acid. This dibromo-anthanthrone has previously been prepared from 5-bromonaphthastyril by Corbellini and Barbaro (*Giorn. Chim. ind. appl.*, 1933, **15**, 335).



(III.) (IV.) (V.) (VI.)

An isomeric 2 : 7-*dibromoanthanthrone* has also been synthesised (see p. 1102) by coupling two molecules of *methyl* 1 : 6-*dibromo-2-naphthoate* in presence of copper bronze, followed by treatment with chlorosulphonic acid. This dyes cotton a bright orange-brown colour in contrast to the pinker shade given by the 4 : 9-derivative.

EXPERIMENTAL.

The method of carrying out the Ullmann reactions and of working up the products is illustrated in the following case.

Methyl 8-bromo-1-naphthoate (4 g.) and methyl *o*-iodobenzoate (8 g., 2 mols.) were melted together with efficient stirring in a small stoppered flask immersed in an oil-bath at 180°. Copper bronze (4 g.) was added in small portions during 30 minutes, and stirring continued for a further 4 hours; the mixture was then cooled and extracted with 200 c.c. of acetone (in four portions), and copper and cuprous halide filtered off. Acetone was removed from the extract on the water-bath, and ether (40—50 c.c.) added; methyl 8-*o*-carbomethoxyphenyl-1-naphthoate then separated. It was filtered off and washed with a little ether. Weight, 2·75 g.; m. p. 131—132°.

This product was heated for 4 hours at 50° with concentrated sulphuric acid (40 c.c.), and the mixture cooled and poured into water. The yellow solid obtained was warmed with dilute alkali solution, leaving insoluble methyl *meso*benzanthrone-8-carboxylate (1·63 g.), m. p. 158—159°; acidification of the orange filtrate gave *meso*benzanthrone-8-carboxylic acid (0·8 g.), m. p. 270—272°.

The ethereal filtrate from the above mixed esters was freed from solvent, and the residue heated with 100 c.c. of concentrated sulphuric acid for 4 hours at 50°. After pouring into water an alkali-insoluble fraction (0·91 g.) was obtained containing anthanthrone and benzanthrone-8-carboxylic ester. The latter component was extracted with alcohol, giving 0·66 g., m. p. 157—159°, and leaving a residue of anthanthrone (0·25 g.) (total yield of benzanthrone derivatives, 75%; anthanthrone, 11%). The relative proportions of benzanthronecarboxylic acid and ester could be altered at will within wide limits by varying the length and temperature of the sulphuric acid treatment of the mixed esters.

Benzanthronecarboxylic acids were decarboxylated in boiling quinoline solution at 240° for 10—15 minutes in the presence of copper bronze. Cyclisation to 3′ : 8-keto*meso*benzanthrones was effected by phosphoric oxide in molten phthalic anhydride (Bigelow and Rule, *loc. cit.*).

With one exception the substituted naphthoic esters employed have already been described (J., 1934, 168, 171), and further reference need only be made to the following starting materials.

5 : 8-Dibromo-1-naphthoic acid has been obtained more readily and in greater yield by

boiling 8-bromo-1-naphthoic acid (30 g.) with glacial acetic acid (100 c.c.) and bromine (30 g.) under reflux for 4—5 hours. Almost pure dibromo-acid (34 g., 86% of the theoretical) is deposited on cooling, m. p. 230—232°.

Methyl 5-*bromo*-2-*iodobenzoate*, prepared in 77% yield from the corresponding acid, m. p. 158—159°, by means of methyl alcohol and sulphuric acid, crystallised from methyl alcohol in colourless needles, m. p. 45—46° (Found by sodium peroxide method : I, 37·0. $C_8H_8O_2BrI$ requires I, 37·2%).

6-Nitrophthalamic acid (Kahn, *Ber.*, 1902, **35**, 3863) was converted by means of sodium hypochlorite solution into 6-nitroanthranilic acid, m. p. 189° (decomp.) (Found : N, 15·6. Calc. for $C_7H_6O_4N_2$: N, 15·3%) [Kahn, *loc. cit.*, records m. p. 180° (decomp.)], and thence into 2-*iodo*-6-*nitrobenzoic acid*, Witt's method of diazotisation with potassium metabisulphite and fuming nitric acid giving a much purer product than could be obtained by use of sulphuric acid and sodium nitrite. Yield, 77% ; m. p. 188—189° (from water) (Found : N, 5·05. $C_7H_4O_4NI$ requires N, 4·8%). *Methyl* 2-*iodo*-6-*nitrobenzoate* was best prepared by boiling the silver salt and methyl iodide under reflux for 3 hours. Yield, 80% ; m. p. 94° (from methyl alcohol) (Found : N, 4·7. $C_8H_6O_4NI$ requires N, 4·6%). A considerable amount of tar was formed during an attempted esterification with thionyl chloride.

The succeeding paragraphs give a brief account of the *meso*benzanthrones and anthanthrones synthesised. The intermediate phenylnaphthyl- and dinaphthyl-carboxylates, where isolated, are described before the cyclised products to which they are related.

Methyl 5-*bromo*-8-(o-*carbomethoxyphenyl*)-1-*naphthoate* formed colourless needles from ligroin, m. p. 155° (Found : Br, 19·9. $C_{20}H_{15}O_4Br$ requires Br, 20·0%).

Methyl 1′-*bromo*meso*benzanthrone*-8-*carboxylate* crystallised in pale yellow needles from alcohol, m. p. 194° (Found : Br, 21·6. $C_{19}H_{11}O_3Br$ requires Br, 21·8%).

1′-*Bromo*meso*benzanthrone*-8-*carboxylic acid*, crystallised from alcohol and eventually from nitrobenzene, formed fine yellow needles, m. p. 315—316° (Found : Br, 22·3. $C_{18}H_9O_3Br$ requires Br, 22·6%).

1′-Bromo*meso*benzanthrone crystallised from chlorobenzene and finally from alcohol in yellow plates, m. p. 176—177°, unchanged on admixture with the direct bromination product of *meso*benzanthrone of the same m. p.

1′-*Bromo*-3′ : 8-*keto*meso*benzanthrone* formed fine orange needles from acetic acid. Yield, 84% ; m. p. 326—328°, sintering at 200°, resolidifying at 326°, and thereafter melting at 325—327° without sintering * (see p. 1099) (Found : C, 64·2; H, 2·0; Br, 24·3. $C_{18}H_7O_2Br$ requires C, 64·5; H, 2·1; Br, 23·9%). It is only sparingly soluble in hot alkaline hyposulphite, forming a yellow suspension in a greenish-brown liquid. Alkalis only attack the ketonic bridge on prolonged boiling (10% aqueous sodium hydroxide dissolves about 40% after 48 hours), giving an inseparable mixture, presumably of *meso*benzanthrone-3′- and -8-carboxylic acids.

The *lactone* of 1′-*bromo*-3′-*hydroxy*meso*benzanthrone*-8-*carboxylic acid* was obtained by oxidising the bromo-acid with chromic oxide (compare Bigelow and Rule, *loc. cit.*). It crystallised from chlorobenzene in pale yellow needles, m. p. 321—323° (yield, 53%) (Found : C, 61·3; H, 2·0. $C_{18}H_7O_3Br$ requires C, 61·55; H, 2·0%). The compound is insoluble in cold alkali, but dissolves slowly on warming to give a purple solution with a red fluorescence. The original lactone is recovered on acidification.

Methyl 4 : 4′-dibromo-1 : 1′-dinaphthyl-8 : 8′-dicarboxylate was isolated from the Ullmann reaction with the mixed esters, and also in 55% yield from 5 : 8-dibromo-1-naphthoic ester and copper bronze at 210—220°. It formed colourless plates, m. p. 205°, from acetone (Corbellini and Barbaro, *loc. cit.*, found m. p. 204·5—205°, having prepared the ester from 5-bromonaphthastyril). When heated with sulphuric acid for 1 hour at 100°, the ester was quantitatively converted into 4 : 9-dibromoanthanthrone, which crystallised in deep red needles from nitrobenzene and functioned as an orange-red vat dye. When the sulphuric acid treatment of the ester (1·5 g.) was limited to 10 minutes at 50°, an orange precipitate was obtained on dilution with water. This was warmed with dilute alkali to remove any acidic compound; the filtrate, however, was not coloured and deposited no solid on acidification. The residue was extracted with hot acetone (30 c.c.) to remove unchanged starting material, leaving an orange residue of *methyl dibromobenzo*meso*benzanthronecarboxylate* (0·75 g.) in which only one of the two carboxyl groups originally present had undergone ring closure. This crystallised from acetic acid in square, deep orange

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* The product obtained by direct bromination of keto*meso*benzanthrone behaves similarly (J. L. Grieve, in these laboratories).

plates, m. p. 233° (Found : Br, 32·3. $C_{23}H_{12}O_3Br_2$ requires Br, 32·2%). The compound acts as an orange vat dye.

Methyl 7 : 8-*benzo*meso*benzanthrone*-4'-*carboxylate*, prepared in a similar way (3 minutes at 50°) by sulphuric acid treatment of the unbrominated 1 : 1'-dinaphthyl-8 : 8'-dicarboxylic ester in 50% yield, formed stout yellow needles, m. p. 154°, from alcohol (Found : C, 81·4; H, 4·2. $C_{23}H_{14}O_3$ requires C, 81·7; H, 4·2%).

6-*Bromo*meso*benzanthrone*-8-*carboxylic acid* formed yellow needles, m. p. 315—316°, from alcohol or nitrobenzene (Found : Br, 22·7. $C_{18}H_9O_3Br$ requires Br, 22·6%).

6-Bromo*meso*benzanthrone (55% yield) separated from alcohol or chlorobenzene in yellow plates, m. p. 182—183°.

6-*Bromo*-3' : 8-*keto*meso*benzanthrone* (84% yield) formed orange needles, m. p. 239—240° (sintering at 230°), from acetic acid (Found : C, 64·4; H, 2·1. $C_{18}H_7O_2Br$ requires C, 64·5; H, 2·1%).

1' : 6-*Dibromo*meso*benzanthrone*-8-*carboxylic acid* formed yellow needles, m. p. 354—356° (decomp.), from nitrobenzene (Found : Br, 36·7. $C_{18}H_8O_3Br_2$ requires Br, 37·0%).

1' : 6-Dibromo*meso*benzanthrone (50% yield) was deposited from chlorobenzene in long yellow needles, m. p. 255—256°, unchanged on admixture with the dibromobenzanthrone, m. p. 255—256°, obtained by boiling the 1'-bromo-compound (1 g.) with bromine (0·6 g.) in aqueous suspension for 3 hours.

1' : 6-*Dibromo*-3' : 8-*keto*meso*benzanthrone* (90% yield) separated from chlorobenzene in fine red needles, m. p. 299—300° (Found : C, 52·2; H, 1·45. $C_{18}H_8O_2Br_2$ requires C, 52·2; H, 1·60%), soluble in sulphuric acid to a purple-red solution with blue fluorescence.

Methyl 5-*nitro*-8-o-*carbomethoxyphenyl*-1-*naphthoate* formed pale yellow needles, m. p. 154—155°, from ligroin (Found : N, 4·1. $C_{20}H_{15}O_6N$ requires N, 3·8%).

1'-*Nitro*meso*benzanthrone*-8-*carboxylic acid* crystallised in golden-yellow needles, m. p. 310° (decomp.) from acetic acid or nitrobenzene (Found : N, 3·8. $C_{18}H_9O_5N$ requires N, 4·4%).

1'-*Nitro*meso*benzanthrone* formed brown crystals, m. p. 248—249°, from toluene and did not depress the m. p. of the yellow 1'-nitro-derivative obtained by nitration of benzanthrone in nitrobenzene solution. The brown colour of the decarboxylation product appears to be due to the presence of a trace of colouring matter and is characteristic of the nitro-compounds prepared in this manner.

1'-*Nitro*-3' : 8-*keto*meso*benzanthrone* (85% yield) separated in orange needles, m. p. 282—283° (sintering at 265°), from chlorobenzene (Found : N, 4·45. $C_{18}H_7O_4N$ requires N, 4·65%). It formed a purple-red solution in cold sulphuric acid.

6-*Nitro*meso*benzanthrone*-8-*carboxylic acid* formed yellow leaflets, m. p. 286—287° (decomp.), from nitrobenzene (Found : N, 3·9. $C_{18}H_9O_5N$ requires N, 4·4%).

6-*Nitro*meso*benzanthrone* crystallised in brownish needles, m. p. 291—292°, from acetic acid (Found : N, 4·8. $C_{18}H_9O_3N$ requires N, 5·1%). The m. p. was depressed to 255—285° by the direct (2'-) nitration product, m. p. 305—307°, obtainable from *meso*benzanthrone. The solution in sulphuric acid was yellow with bright green fluorescence.

6-*Nitro*-3' : 8-*keto*meso*benzanthrone* formed deep orange needles, m. p. 316—317°, from chlorobenzene (Found : N, 4·25. $C_{18}H_7O_4N$ requires N, 4·65%). The yield obtained by the phthalic anhydride method was only 58% owing to the deposition of dark material which occluded some of the reactants. Dehydration in boiling nitrobenzene solution with phosphoric oxide (2 hours) gave a yield of 79%.

No homogeneous unsymmetrical products or their corresponding benzanthrone derivatives could be isolated from the Ullmann reaction between methyl 8-bromo-1-naphthoate and (*a*) methyl 2 : 4-dibromobenzoate, (*b*) methyl 2-iodo-4-nitrobenzoate, (*c*) methyl 2-iodo-6-nitrobenzoate, or between (*d*) methyl 8-bromo-5-nitro-1-naphthoate and methyl 2-iodo-5-nitrobenzoate, or (*e*) methyl 8-bromo-4 : 5-dinitro-1-naphthoate and methyl *o*-iodobenzoate.

Synthesis of 2 : 7-*Dibromoanthanthrone*.—1 : 6-Dibromo-2-naphthylamine was most satisfactorily prepared from benzylidene-β-naphthylamine in two stages (cf. Franzen and Eidis, *J. pr. Chem.*, 1913, **88**, 755). Yield, 74%; m. p. 122—123°. Trouble was encountered in applying the Sandmeyer reaction to the dibromo-amine, owing to the low solubility of the salts and the formation of an insoluble brown diazo-complex due to the diazotised base coupling with itself. The former difficulty was overcome by grinding the base to a fine suspension in hydrochloric acid, and the latter by reducing the acid concentration. 1 : 6-Dibromo-2-naphthylamine (60 g.) in a mixture of 60 c.c. of concentrated hydrochloric acid and 200 c.c. of water was reduced to a fine suspension by milling in a rotating bottle; the mixture was then diluted to 600 c.c. and stirred at 0° while sodium nitrite (15 g.) in 45 c.c. of water was added during 5 minutes with addition of ice. Stirring was continued for 15 minutes and the yellow solution was then filtered from brown insoluble material (3 g.) and added slowly with stirring at 10° to a solution of cuprous cyanide (prepared from 90 g. of sodium cyanide in 400 c.c. of water, and 60 g. of copper sulphate crystals in 400 c.c. of water). Vigorous effervescence occurred and a light brown solid was deposited. After further stirring for 1 hour in the cold and another hour on the water-bath, the product was filtered off and washed. Yield, 59 g. The crude nitrile was boiled for 24 hours with a mixture of water (100 c.c.), sulphuric acid (200 c.c.), and glacial acetic acid (400 c.c.). On pouring into 3 l. of cold water a solid was obtained from which the dibromo-acid was extracted with hot dilute alkali, giving 33 g. of 1 : 6-dibromo-2-naphthoic acid, m. p. 235—240°. Crystallisation from nitrobenzene afforded 28 g. (42%) of pure acid, m. p. 249—250°.

Methyl 1 : 6-*dibromo*-2-*naphthoate*, prepared by use of thionyl chloride, crystallised from alcohol in colourless needles, m. p. 99—100°. Yield, almost quantitative (Found : Br, 46·8. $C_{12}H_8O_2Br_2$ requires Br, 46·5%).

The methyl ester (15 g.) was heated with copper bronze (10 g.) for 3 hours at 160—170°, the resulting paste extracted with acetone, and the extract concentrated until crystallisation set in. On filtration this gave 5·0 g. (41%) of *methyl* 6 : 6′-*dibromo*-1 : 1′-*dinaphthyl*-2 : 2′-*dicarboxylate*, which crystallised from acetone in rectangular plates, m. p. 220° (Found : Br, 30·6. $C_{24}H_{16}O_4Br_2$ requires Br, 30·3%). A somewhat lower yield was obtained by effecting dehalogenation in boiling xylene during a longer time.

Cyclisation of the dinaphthyldicarboxylic ester presented unexpected difficulty, treatment with sulphuric acid leading to extensive sulphonation. The ester was therefore hydrolysed with the above acetic acid and sulphuric acid mixture (4 hours), affording a high yield of practically pure 6 : 6′-*dibromo*-1 : 1′-*dinaphthyl*-2 : 2′-*dicarboxylic acid*, which separated from nitrobenzene in colourless plates, m. p. 342—344° (decomp.) (Found : Br, 31·6. $C_{22}H_{12}O_4Br_2$ requires Br, 32·0%). Although the corresponding acid chloride could not be cyclised by use of aluminium chloride in nitrobenzene at 100°, partial conversion into an impure anthanthrone was achieved by heating the acid with molten phthalic anhydride and phosphoric oxide at 200°. Chlorosulphonic acid, however, proved to be a most effective reagent for this purpose. The dicarboxylic acid (2 g.) was heated with redistilled chlorosulphonic acid (25 c.c.) for 30 minutes at 50°. On pouring into water, 2 : 7-*dibromoanthanthrone*, m. p. above 360°, was obtained in good yield. The orange-coloured solid gives a green solution in sulphuric acid and a deep violet vat with alkaline hyposulphite, which dyes cotton a deep orange colour. In boiling nitrobenzene it dissolves sparingly, depositing orange needles on cooling (Found : Br, 34·7. $C_{22}H_8O_2Br_2$ requires Br, 34·5%).

The authors thank the Carnegie Trust for a Scholarship (to F. R. S.) and a Teaching Fellowship (to H. G. R.). They are also indebted to Imperial Chemical Industries, Ltd., for materials and a grant.

EDINBURGH UNIVERSITY. [*Received, April* 21*st*, 1937.]