299. 1 : 9-*Pyrazoloanthrone.** *Part I. Replacement of Halogens in Derivatives of* 1 : 9-*Pyrazoloanthrone.*

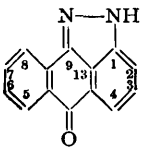
By William Bradley and Kenneth W. Geddes.

The 2- and 3-bromo- and 4-, 5-, and 8-chloro-derivatives of 1 : 9-pyrazoloanthrone * have been prepared and their behaviour towards aniline, piperidine, and sodium methoxide investigated. The relation between orientation and ease of replacement of a substituent is similar to that which obtains in the *meso*benzanthrone series. The two *N*-methyl derivatives of 1 : 9-pyrazoloanthrone have been prepared and several of their halogeno-drivatives. The properties of the halogen compounds are generally similar to those of the parent 1 : 9-pyrazoloanthrone.

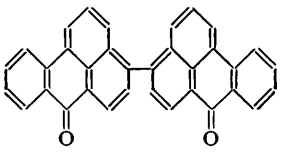
1 : 9-Pyrazoloanthrone * (I) resembles *meso*benzanthrone in its ability to undergo self-condensation. When heated with alcoholic potassium hydroxide, *meso*benzanthrone affords di*meso*benzanthron-4-yl (II) (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259), and in similar circumstances 1 : 9-pyrazoloanthrone yields di-(1 : 9-pyrazoloanthron-2-yl) (III) (Mayer and Heil, *Chem.-Ztg., Fortschrittsber.*, 1929, p. 56).

* The systematic name for a substance of structure (I) would be pyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone, and that for the isomer with hydrogen attached to the other nitrogen atom would be pyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone. Although formula (I) is used in this paper the position of the hydrogen atom cannot be allocated, and the less determinate name, 1 : 9-pyrazoloanthrone is therefore used. Ed.

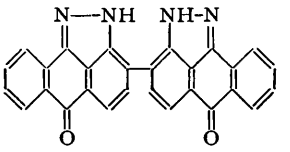
With *meso*benzanthrone the capacity for self-condensation is related to its ability to undergo direct substitution by bases, including the anions of weak acids, and to the ease with which halogen substituents are replaced at positions 4 and 6 (Bradley, *J.*, 1937, 1091; 1948, 1175; Bradley and Jadhav, *J.*, 1937, 1791; 1948, 1622, 1748). For the latter reason it was of interest to study the replacement of halogen substituents in derivatives of 1 : 9-pyrazoloanthrone.



(I)



(II)

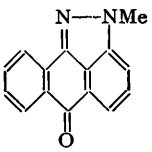


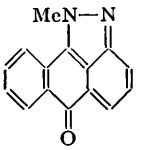
(III)

Of the several routes to 1 : 9-pyrazoloanthrone (cf. B.I.O.S. Report No. 987, p. 128; B.P. 297 366) we found Mohlau's method (*Ber.*, 1912, **45**, 2244) to be the most satisfactory. Mohlau described the preparation of 8-chloro-1 : 9-pyrazoloanthrone, and we have used the same procedure in preparing the 2- and 3-bromo- and 4- and 5-chloro-derivatives.

An 8-chloro-substituent proved inert towards various bases, one in position 5 was replaced by piperidine, but not by sodium methoxide or aniline; a 4-chloro-substituent was replaced by each of the three reagents, and by hydrazine. The halogen substituent of 2-bromo-1 : 9-pyrazoloanthrone was replaced by piperidine and sodium methoxide, but that of the 3-bromo-isomer was inert. The results harmonise with those obtained earlier with *meso*benzanthrone in which it was found that halogen substituents situated *ortho* or *para* to the carbonyl group may be replaced. In addition the effect of the carbonyl group is transmitted more easily through the indazole nucleus of 1 : 9-pyrazoloanthrone than through the other benzene nucleus.

Attention has also been given to the two *N*-methyl-1 : 9-pyrazoloanthrones (IV and V), because they should exhibit different degrees of nuclear reactivity. The formation of a methyl derivative, m. p. 221—224°, by methyl alcohol and sulphuric acid was recorded in G.P. 454 760. Later G.P. 456 763 and 479 284 mentioned the formation of two methyl derivatives when sodium hydroxide and methyl sulphate were used. A methyl derivative, m. p. 189°, was prepared by the action of methylhydrazine on 1-chloroanthraquinone (B.P. 470 475). We have confirmed the formation of the compound, m. p. 189°, and regard it as 1'-methylpyrazolo(5' : 4' : 3'-1 : 13 : 9)anthrone (IV) because Blanksma and Wackers (*Rec. Trav. chim.*, 1936, **55**, 655) found that methylhydrazine reacts at the secondary amine group with picryl chloride and 1-chloro-2 : 4-dinitrobenzene.

(IV)




(V)

Repeating the methylation of 1 : 9-pyrazoloanthrone with sodium hydroxide and methyl sulphate and separating the alkali-insoluble products by chromatography we obtained two derivatives, (*a*) m. p. 189°, identical with that mentioned above, and (*b*) m. p. 229°, which appeared to be a purer form of the product, m. p. 221—224°. The constitution (IV) having been assigned, the isomer, m. p. 229°, must be 1'-methylpyrazolo-(3' : 4' : 5'-1 : 13 : 9)anthrone (V). Maki and Akamastsu (Ann. Meeting Soc. Chem. Ind. Japan, 1949; Rep. Jap. Assoc. Promotion Sci., 1949) reported *N*-methyl derivatives, m. p. 189° and 154·5°, respectively. Whilst the former is the compound (IV) we have obtained some of the isomer, m. p. 229°, from the product of m. p. 154·5°.

Using Mohlau's method (*loc cit.*), but methylhydrazine instead of hydrazine, we have prepared 2-methyl- and 3-bromo-derivatives of (IV). An attempt to prepare (IV) by reducing the *N*-nitroso-derivative of 1-methylaminoanthraquinone (G.P. 442 312) was unsuccessful.

Bromination of (V) gave the 2-bromo-derivative identical with one of the products

obtained by methylating 2-bromo-1 : 9-pyrazoloanthrone with alkali and methyl sulphate. Bromination of (IV) occurred at position 4.

4-Bromo-1'-methylpyrazolo(5' : 4' : 3'-1 : 13 : 9)anthrone heated with methanolic sodium methoxide afforded the corresponding 4-hydroxy-derivative, also obtained by the action of alkali hydroxides on 4-chloro-1'-methylpyrazolo(5' : 4' : 3'-1 : 13 : 9)anthrone which was prepared from 1 : 4-dichloroanthraquinone by methylhydrazine. In its reaction with sodium methoxide the 4-bromo-derivative of (IV) resembles the similarly constituted 6-chloro*meso*benzanthrone which yields 6-hydroxy*meso*benzanthrone in similar circumstances. In contrast, the 2-bromo- and the 4-chloro-derivative of 1 : 9-pyrazoloanthrone afford the corresponding methoxy-compounds with the same reagent.

Experimental

1 : 9-Pyrazoloanthrone was prepared from 1-chloroanthraquinone by the hydrazine method (Mohlau, *loc. cit.*).

1 : 2-*Dibromoanthraquinone*.—1-Amino-2-bromoanthraquinone (50 g.) (Grandmougin, *Compt. rend.*, 1921, **173**, 839) was stirred at room temperature during 4 hours with a solution prepared from sodium nitrite (18 g.) and concentrated sulphuric acid (150 c.c.). The product was added to ice, and the precipitated diazonium salt collected and added to a suspension of cuprous bromide in 50% (w/w) hydrobromic acid (200 c.c.). [The cuprous bromide was prepared from copper sulphate (180 g.), sodium bromide (120 g.), and sodium sulphite (50 g.).] Nitrogen was liberated, and the suspension was warmed for a few minutes to complete the reaction and then mixed with water. The precipitate was collected, stirred with warm dilute nitric acid, then separated, washed, and dried. Recrystallisation from chlorobenzene gave pale yellow needles (39·5 g.), m. p. 223° (Battegay, *Bull. Soc. chim.*, 1921, [iv], **29**, 1017, records m. p. 223°).

2-*Bromo*-1 : 9-*pyrazoloanthrone*.—Hydrazine hydrate (4·25 g. of a 50% solution) was added to a solution containing 1 : 2-dibromoanthraquinone (8·5 g.) in pyridine (150 c.c.). Heating under reflux caused a deep red colour to develop, changing to yellow after 5 hours. The product was added to water, and the precipitate was collected, washed, dried (7 g.; m. p. 265—272°), and then recrystallised from nitrobenzene. The resulting brown solid, m. p. 285—287°, was further purified by vacuum-sublimation or by chromatography on alumina and obtained as yellow needles, m. p. 289—290° (Found : C, 56·4; H, 2·35; N, 9·7; Br, 27·5. $C_{14}H_7ON_2Br$ requires C, 56·2; H, 2·5; N, 9·4; Br, 26·7%). 2-*Bromo*-1 : 9-*pyrazoloanthrone* forms an orange solution in aqueous sodium hydroxide, changed to greenish-yellow on addition of sodium dithionite. The pale greenish-yellow solution in pyridine becomes pink on addition of a drop of concentrated methyl alcoholic potassium hydroxide (Bradley and Leete, *J.*, 1951, 2132). The compound forms an orange solution in concentrated sulphuric acid. The *N*-acetyl derivative had m. p. 205° (from chlorobenzene); G.P. 457 182 records m. p. 209—211°.

3-*Bromo*-1 : 9-*pyrazoloanthrone*.—Prepared from 1 : 3-dibromoanthraquinone (12 g.) and hydrazine hydrate (6 g. of a 50% aqueous solution) this *compound* had m. p. 273—279° (yield, 10 g.). Recrystallisation from chlorobenzene gave yellow, minute needles, m. p. 309—310° (Found : N, 9·1. $C_{14}H_7ON_2Br$ requires N, 9·4%). It dissolves with an orange colour in aqueous sodium hydroxide; a greenish-yellow solution results on addition of sodium dithionite. The greenish-yellow solution in pyridine becomes yellowish-pink on the addition of methyl alcoholic potassium hydroxide, and a yellow fluorescence develops.

The *N*-acetyl derivative crystallised when 3-bromo-1 : 9-pyrazoloanthrone (10 g.) was heated under reflux for 10 minutes with acetic anhydride (10 c.c.). The pale yellow needles were collected, washed with alcohol, and dried, and had m. p. 222—224° (8·5 g.). Recrystallisation from chlorobenzene gave pale yellow, minute needles, m. p. 228°.

4-*Chloro*-1 : 9-*pyrazoloanthrone*.—Prepared according to B.P. 345 748 from hydrazine hydrate and 1 : 4-dichloroanthraquinone (Ullmann, *Ber.*, 1920, **53**, 826). The product crystallised from chlorobenzene had m. p. 318° (Found : C, 65·7; H, 3·0; N, 10·7; Cl, 14·15. Calc. for $C_{14}H_7ON_2Cl$: C, 65·9; H, 2·8; N, 11·0; Cl, 14·0%). B.P. 345 748 records m. p. 301—302°. The orange solution in aqueous sodium hydroxide becomes yellow on the addition of sodium dithionite. The pale yellow solution in pyridine changes to orange and develops a green fluorescence on the addition of methyl alcoholic potassium hydroxide. It forms an orange solution in concentrated sulphuric acid.

5-*Chloro*-1 : 9-*pyrazoloanthrone*.—1 : 5-Dichloroanthraquinone (20 g.), hydrazine hydrate (5 g.), and pyridine (175 c.c.) were heated under reflux for 5 hours, and then the product (m. p. 240—245°; 18·8 g.) was isolated. It was dissolved in concentrated sulphuric acid, heated to

100°, and then recovered (m. p. 275—285°) by addition of the mixture to water. Recrystallisation from chlorobenzene gave golden-yellow flakes, m. p. 298° (Found : C, 65·5; H, 3·0; N, 11·0; Cl, 14·4. $C_{14}H_7ON_2Cl$ requires C, 65·9; H, 2·8; N, 11·0; Cl, 14·0%). It resembled the isomeric 4-chloro-derivative in its colour reactions with sodium hydroxide, alkaline sodium dithionite, pyridine and methyl alcoholic potassium hydroxide, and concentrated sulphuric acid.

The compound (8 g.) was heated for 20 minutes with acetic anhydride (50 c.c.). On cooling, the *acetyl* derivative crystallised in brown needles, m. p. 249° (Found : N, 9·9; Cl, 11·6. $C_{16}H_9O_2N_2Cl$ requires N, 9·4; Cl, 11·9%).

8-*Chloro*-1 : 9-*pyrazoloanthrone.*—Prepared by Mohlau's method (*loc. cit.*), the product crystallised from xylene in yellow needles, m. p. 346—347° (Found : N, 11·0. Calc. for $C_{14}H_7ON_2Cl$: N, 11·0%). Mohlau records m. p. >360°.

The *acetyl* derivative (7 g.) separated when 8-chloro-1 : 9-pyrazoloanthrone (8 g.) was refluxed for 10 minutes with acetic anhydride (60 c.c.). Recrystallisation from chlorobenzene gave pale yellow needles, m. p. 280° (Found : C, 64·3; H, 3·0; N, 9·5; Cl, 12·3. $C_{16}H_9O_2N_2Cl$ requires C, 64·5; H, 3·1; N, 9·4; Cl, 11·9%).

Methylation of 1 : 9-*Pyrazoloanthrone.*—(*a*) 1 : 9-Pyrazoloanthrone (11 g.) was treated with methyl sulphate (25 g.), sodium hydroxide (10·5 g.), water (100 c.c.), and alcohol (50 g.) according to G.P. 479 284. The product (10·1 g.; m. p. 152—162°) could not be purified satisfactorily by crystallisation from alcohol or chlorobenzene. The product (10 g.) was chromatographed in benzene on alumina. A broad yellow band formed was eluted by 100-c.c. portions of benzene. The several extracts were collected and evaporated, yielding : (i) 1'-Methylpyrazolo(5' : 4' : 3'-1 : 13 : 9)anthrone, yellow needles, m. p. 189° (Found : C, 76·7; H, 4·4; N, 11·6. Calc. for $C_{15}H_{10}ON_2$: C, 76·9; H, 4·3; N, 12·0%) (5·4 g.). These dissolved in benzene forming a yellow solution having a vivid blue fluorescence. They were insoluble in aqueous sodium hydroxide ; on addition of sodium dithionite a pale yellow solution was formed. The yellow solution in pyridine remained unaltered on addition of solid potassium hydroxide. The same reagent added to a solution in acetone caused a slow change to dull red. (ii) 1'-Methylpyrazolo(3' : 4' : 5'-1 : 13 : 9)anthrone, yellow needles, m. p. 229° (Found : C, 76·6; H, 4·1; N, 12·1%), which afforded a yellow solution with a bright yellowish-green fluorescence in benzene. The behaviour with sodium hydroxide, sodium dithionite, and pyridine–potassium hydroxide was identical with that of the isomer. Its yellow solution in acetone, however, changed rapidly through red and violet to blue on the addition of alkali. (iii) A mixture, m. p. 150—160° (1·6 g.), from the middle of the column.

(*b*) 1 : 9-Pyrazoloanthrone (20 g.) was treated with methyl alcohol (30 g.) and concentrated sulphuric acid (120 g.) as described in G.P. 454 760. The product (13 g.) crystallised from chlorobenzene as yellow needles, m. p. 224° (Found : C, 76·5; H, 4·1; N, 12·4%), identical in its reactions with the isomer (ii), m. p. 229°.

(*c*) 1-Chloroanthraquinone (7·5 g.) was treated for 12 hours with methylhydrazine sulphate (5 g.) in pyridine (75 c.c.) containing anhydrous potassium carbonate (7 g.), according to the procedure of B.P. 470 475. The product (7 g.), m. p. 151—156°, crystallised from chlorobenzene as yellow needles (5 g.), m. p. 187—189° (Found : C, 76·9; H, 4·6; N, 11·6%), which did not depress the m. p. of the isomer (i).

In a second preparation, the constituents of the pyridine mother-liquor obtained at the first stage were examined. Addition of water gave a yellow solid (3·5 g.) which crystallised from alcohol (m. p. 141—143°). Chromatography from benzene on alumina afforded material, m. p. 151—152° (Found : N, 6·2; Cl, 7·8%), which gave the reactions of an anthraquinone derivative and melted at 160—170° when mixed with the isomer, m. p. 189°.

1-N-*Methyl*-N-*nitrosoaminoanthraquinone.*—1-Methylaminoanthraquinone afforded the N-*nitroso*-derivative with sodium nitrite and acetic acid (G.P. 422 312). This crystallised from chlorobenzene as golden yellow needles, m. p. 185—186° (Found : C, 67·8; H, 3·6; N, 10·4. $C_{15}H_{10}O_3N_2$ requires C, 67·7; H, 3·8; N, 10·5%), and gave a positive Liebermann reaction. When heated with alcohol (150 c.c.) and sodium sulphide (2 g.) for 1·5 hours it (2 g.) gave 1-methylaminoanthraquinone, m. p. 169—170°, not depressed by admixture with the authentic compound. The same compound resulted when the nitrosamine (1·5 g.) was heated under reflux for 6 hours with pyridine (40 c.c.) containing hydrazine hydrate (0·7 g.). Finally, the nitrosamine (3 g.), stirred with zinc dust (10 g.) and a mixture of acetic acid (100 g.) and water (100 g.) at 20°, yielded a product, m. p. 150—152°, consisting mainly of 1-methylaminoanthraquinone.

2-*Bromo*-1'-*methylpyrazolo*(5' : 4' : 3'-1 : 13 : 9)*anthrone.*—1 : 2-Dibromoanthraquinone (4 g.), methylhydrazine sulphate (2·5 g.), pyridine (40 c.c.), and sodium acetate (3 g.) were refluxed for

10 hours. Next morning the precipitate was collected, washed with water, and dried (1 g.; m. p. 206—207°). Vacuum-sublimation gave a yellow *compound*, m. p. 224—227° (Found : N, 9·1; Br, 25·2. $C_{15}H_9ON_2Br$ requires N, 8·9; Br, 25·6%), not depressed on admixture with the compound, m. p. 230°, obtained as fraction (i) in the methylation of 2-bromo-1 : 9-pyrazoloanthrone (see below).

2-*Bromo*-1′-*methylpyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)*anthrone*.—A solution of bromine (1·5 g.) in acetic acid (10 c.c.) was added slowly, with stirring, to one of 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (2 g.) in acetic acid (20 c.c.). After 2 hours at the room temperature a yellow solid had separated, and this was collected, washed free from acid, and dried (2·1 g., m. p. 198—226°). Recrystallisation from chlorobenzene gave the *bromo*-compound as yellow crystals, m. p. 232—234° (Found: N, 8·9; Br, 26·0%).

Methylation of 2-*Bromo*-1 : 9-*pyrazoloanthrone*.—Methyl sulphate (17 g.) was stirred for 3 hours at the room temperature with a solution of 2-bromo-1 : 9-pyrazoloanthrone (10 g.) and sodium hydroxide (7 g.) in water (70 c.c.). The product which separated was collected, digested with a solution of sodium hydroxide in aqueous ethyl alcohol, then washed, and dried (9 g.; m. p. 185—190°), and a portion (5 g.) was chromatographed from benzene on alumina. A broad yellow band formed, becoming brownish-yellow at the top of the column. Benzene was passed through the column, and each successive 200 c.c. of eluate was concentrated to crystallisation. The following fractions resulted, in order : (i), m. p. 230° (0·6 g.); (ii), m. p. 226—229° (1·2 g.); (iii), m. p. 180—190° (1·9 g.); (iv), m. p. 170—185° (0·2 g.); (v), m. p. 180—216° (0·2 g.); (vi), m. p. 226—232° (0·1 g.). Fraction (vi) (Found : N, 8·9%) did not depress the m. p. of the preceding product, m. p. 232—234°. Fraction (i) (Found : C, 57·3; H, 3·2; N, 8·9; Br, 25·4%) was identical with the product obtained from 1 : 2-dibromoanthraquinone (see above).

3-*Bromo*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—1 : 3-Dibromoanthraquinone (10 g.), methylhydrazine sulphate (5 g.), pyridine (125 c.c.), and potassium carbonate (7 g.) were refluxed for 12 hours and then kept overnight. The precipitated greenish-yellow needles of the *pyrazoloanthrone* were collected, washed, and dried (4 g.; m. p. 242—244°) (Found : C, 57·5; H, 3·1; N, 8·8; Br, 25·6%).

4-*Chloro*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—Prepared analogously from 1 : 4-dichloroanthraquinone (5 g.), methylhydrazine sulphate (5 g.), sodium carbonate (7 g.), and pyridine (50 c.c.) by 8 hours' refluxing, the *chloro*-compound (2 g.) had m. p. 260° (Found : C, 67·1; H, 3·7; N, 10·8. $C_{15}H_9ON_2Cl$ requires C, 67·1; H, 3·4; N, 10·5%) after sublimation *in vacuo*.

2 : 1′-*Dimethylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—Prepared similarly from 1-chloro-2-methylanthraquinone, the *methyl* analogue crystallised from chlorobenzene as yellow needles, m. p. 217—218° (Found : N, 10·8. $C_{16}H_{12}ON_2$ requires N, 11·2%).

4-*Bromo*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—Bromine (2·5 g.) in acetic acid (10 c.c.) was added to a warm solution of 1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (3 g.) in acetic acid (50 c.c.). After an hour's refluxing the product was added to water, and the yellow precipitate was collected, washed, and dried (2·6 g.; m. p. 170—180°). Repeated crystallisation from chlorobenzene gave this *compound* as yellow, minute needles, m. p. 248—249° (Found : C, 57·8; H, 2·9; N, 9·2; Br, 25·7%).

Replacement Reactions.—4-*Anilino*-1 : 9-*pyrazoloanthrone*. 4-Chloro-1 : 9-pyrazoloanthrone (0·5 g.) and freshly distilled aniline (5 g.) were heated under reflux for 3 hours. On cooling, a pale brown solid separated. It was collected, washed with dilute hydrochloric acid, then water, and finally dried. The product (0·35 g.; m. p. 260—270°) was chromatographed on alumina from benzene. The main band was orange; it was accompanied by pink and blue bands. The orange region was extruded and the adsorbed material extracted with acetone. Evaporation afforded material, m. p. 272—273°, and this crystallised from chlorobenzene in golden-orange needles, m. p. 282—283° (Found : N, 13·4. $C_{20}H_{13}ON_3$ requires N, 13·5%). The *anilino*-compound dissolved in concentrated sulphuric acid to an orange solution. In pyridine it was pale yellow, and orange on the addition of methyl alcoholic potassium hydroxide.

4-*Piperidino*-1 : 9-*pyrazoloanthrone*, prepared similarly by heating 4-chloro-1 : 9-pyrazoloanthrone (0·2 g.) with piperidine (2 g.), crystallised from chlorobenzene as yellow needles, m. p. 264° (Found : N, 13·7. $C_{19}H_{17}ON_3$ requires N, 13·8%). The solution in concentrated sulphuric acid was pale yellow. It formed a bright yellow solution in 20% sodium hydroxide solution, showing a greenish yellow fluorescence; the fluorescence disappeared on addition of sodium dithionite. The yellow solution in pyridine became orange and developed a greenish-yellow fluorescence on addition of potassium hydroxide.

4-*Methoxy*-1 : 9-*pyrazoloanthrone*. 4-Chloro-1 : 9-pyrazoloanthrone (0·5 g.) was heated under reflux for 3 hours with a solution prepared from sodium (2·5 g.) and methanol (25 c.c.).

After cooling, and addition of dilute hydrochloric acid, a pale yellow solid separated. This *methoxy*-derivative was collected, washed, and dried (0·35 g.; m. p. 270—274°), and was obtained by crystallisation from chlorobenzene as a pale yellow solid, m. p. 287—288° (Found : N, 11·0; OMe, 9·8. $C_{15}H_{10}O_2N_2$ requires N, 11·2; OMe, 12·4%). It dissolved in 20% aqueous sodium hydroxide with a yellow colour and a green fluorescence.

4-*Hydrazino*-1 : 9-*pyrazoloanthrone.* Hydrazine hydrate (0·75 g.), pyridine (25 c.c.), and 4-chloro-1 : 9-pyrazoloanthrone were heated at 140° for 10 hours. Brown needles separated, and these were collected, washed, dried (1 g.), and sublimed *in vacuo*. The *product* had m. p. 270° (Found : N, 21·8. $C_{14}H_{10}ON_4$ requires N, 22·4%). It was sparingly soluble in hot water, forming a pale yellow solution with a green fluorescence. It gave a similar solution in pyridine; on addition of methyl alcoholic potassium hydroxide a yellow solution resulted with a bright-orange fluorescence. It was recovered unaltered after being stirred in concentrated sulphuric acid at 90° for 15 minutes.

5-*Piperidino*-1 : 9-*pyrazoloanthrone.* 5-Chloro-1 : 9-pyrazoloanthrone (0·5 g.) and piperidine (5 g.) were heated under reflux for 3 hours. The reddish-orange solution was cooled and added to water, and the orange precipitate collected, washed, and dried (0·4 g.; m. p. 205—210°). Recrystallisation from chlorobenzene gave the *piperidino*-compound as yellow needles, m. p. 218—219° (Found : N, 13·5. $C_{19}H_{17}ON_3$ requires N, 13·8%). It dissolved in concentrated sulphuric acid with a bright yellow, and in sodium hydroxide with a wine-red colour, the latter becoming yellow on the addition of sodium dithionite. The yellow solution in pyridine became pinkish-yellow on addition of methyl alcoholic potassium hydroxide.

5-Chloro-1 : 9-pyrazoloanthrone (0·5 g.) was recovered unaltered after 4 hours' refluxing with a solution of sodium (2·5 g.) in methanol (25 c.c.). Heated with aniline (5 g.) for 3 hours under reflux, 5-chloro-1 : 9-pyrazoloanthrone (0·5 g.) afforded mainly unchanged material (m. p. 220—240° (Found : N, 11·1; Cl, 6·7%).

8-Chloro-1 : 9-pyrazoloanthrone did not react with piperidine at the b. p. during 21 hours, or with aniline at the b. p. during 3 hours.

2-*Piperidino*-1 : 9-*pyrazoloanthrone.* 2-Bromo-1 : 9-pyrazoloanthrone (0·5 g.) heated under reflux for 3 hours with piperidine (5 g.) afforded a product, m. p. 216—250° (0·4 g.), which, after crystallisation from chlorobenzene, had m. p. 251—252° (Found : N, 13·4. $C_{19}H_{17}ON_3$ requires N, 13·8%). This *derivative* dissolved in concentrated sulphuric acid with a pale yellow colour, and in sodium hydroxide with an orange colour becoming yellow on the addition of sodium dithionite. The yellow solution in pyridine exhibited a pale green fluorescence; on addition of methanolic potassium hydroxide the yellow colour deepened and a yellow fluorescence developed.

2-*Methoxy*-1 : 9-*pyrazoloanthrone.* 2-Bromo-1 : 9-pyrazoloanthrone (0·5 g.), heated for 3 hours with a solution of sodium (2·5 g.) in methanol (25 c.c.), afforded 0·4 g. of the *methoxy*-compound, yellow needles, m. p. 224—226° (from chlorobenzene) (Found : N, 10·9; OMe, 10·4. $C_{15}H_{10}O_2N_2$ requires N, 11·2; OMe, 12·4%). It dissolved in aqueous sodium hydroxide with a yellow colour and a green fluorescence.

Action of Reagents on 3-*Bromo*-1 : 9-*pyrazoloanthrone.*—3-Bromo-1 : 9-pyrazoloanthrone was recovered after being heated under an excess of sodium methoxide (4 hours), aniline (3 hours), or piperidine (6 hours). It was also recovered mainly unchanged after 12 hours in boiling ethanolic potassium hydroxide (3·5 g. in 7 c.c.) : a product, m. p. 280—285°, was obtained by vacuum-sublimation of the crude product.

4-*Hydroxy*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone.*—(*a*) 4-Bromo-1′-methylpyrazolo-(5′ : 4′ : 3′-1 : 13 : 9)anthrone (0·4 g.) was heated under reflux with a solution of sodium (4 g.) and methanol (40 c.c.). After addition of water and dilute hydrochloric acid the methanol was distilled off, and the yellow precipitate was collected, washed, and dried (0·3 g.) It was extracted with aqueous sodium hydroxide, and the solution was filtered and then acidified, giving the 4-*hydroxy*-derivative, m. p. 204—205° (Found : N, 11·4. $C_{15}H_{10}O_2N_2$ requires N, 11·2%).

(*b*) The same derivative, m. p. 206—208°, resulted when 4-chloro-1′-methylpyrazolo-(5′ : 4′ : 3′-1 : 13 : 9)anthrone was heated with methanolic sodium methoxide under the same conditions.

With respect to this and the following paper the authors thank the University of Leeds for the award of a Clothworkers Research Scholarship and the Trustees of Messrs. Courtaulds' Scientific and Educational Trust Fund for the award of a grant to one of them (K. W. G.). They also thank Imperial Chemical Industries Limited for intermediates and a grant towards the cost of microanalyses.

Clothworkers Research Laboratory,
University of Leeds. [*Received, December 27th*, 1951.]