300. 1 : 9-*Pyrazoloanthrone. Part II.* Nuclear Substitution by Bases and Self-condensation in* 1 : 9-*Pyrazoloanthrone and its* N-*Methyl Derivatives.*

By William Bradley and Kenneth W. Geddes.

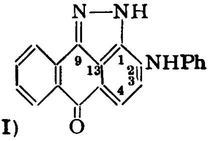
1 : 9-Pyrazoloanthrone and its *N*-methyl derivatives readily undergo nuclear substitution by reactive anions, for example, that of sodium anilide. The substituting anion enters the indazole nucleus and replaces hydrogen in the *para*-position to the carbonyl group. 1′-Methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone is more easily substituted than the isomeric 1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone. The difference is attributed to bond-fixation, which results in a higher degree of unsaturation in the case of the first isomer.

1 : 9-Pyrazoloanthrone and its *N*-methyl derivatives undergo self-condensation in the presence of bases. The constitutions of the products have been determined, and the results have been applied to decide the structures of the products which are obtained by methylating di-(1 : 9-pyrazolo-2-anthronyl). The structural factors which affect the self-condensation have been investigated, and the steps in the condensation process are discussed.

1 : 9-Pyrazoloanthrone and its *N*-methyl derivatives, as well as di-(1 : 9-pyrazolo-2-anthronyl), are hydrolysed by fused alkalis. The constitutions of the resulting acids are considered.

In Part I * it was shown that 1 : 9-pyrazoloanthrone resembles *meso*benzanthrone in the properties of its halogen derivatives. The present communication describes experiments on the direct replacement of nuclear hydrogen in 1 : 9-pyrazoloanthrone by bases, including anions, and the self-union of 1 : 9-pyrazoloanthrone and its *N*-methyl derivatives.

1 : 9-Pyrazoloanthrone reacts with sodium anilide to form 2-anilino-1 : 9-pyrazoleanthrone (I), identical with the compound formed by the action of sodium anilide on 2-bromo-1 : 9-pyrazoloanthrone. A similar compound is formed when the sodium derivative of *o*-toluidine is used. In these reactions 1 : 9-pyrazoloanthrone resembles *meso*benzanthrone (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 258). When heated with potassium hydroxide and an oxidant, *meso*benzanthrone affords a mixture of 4- and 6-hydroxy*meso*benzanthrone (Bradley and Jadhav, *J.*, 1937, 1791). 1 : 9-Pyrazoloanthrone does not behave in this way; the main product is an acid, either (II) or (III). It is probably (II) since ring-opening is dependent on the presence of the indazole nucleus. Heating with sulphuric acid re-forms 1 : 9-pyrazoloanthrone. Alkaline oxidation of 1 : 9-pyrazoloanthrone yields also a small quantity of a phenolic substance, possibly a hydroxy-derivative of (II).



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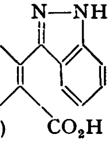

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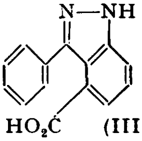
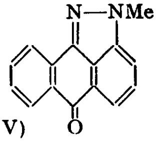


(III)

The *N*-methyl derivative (IV), m. p. 189°, of 1 : 9-pyrazoloanthrone reacted analogously with sodium anilide to form the 2-anilino-derivative (V). Alkaline oxidation of (IV) yielded an acid whence (IV) was regenerated by hot sulphuric acid. The acid was probably (VI) for a reason similar to that already mentioned. It was accompanied by a phenolic product, possibly a hydroxy-derivative of (VI). The *N*-methyl-1 : 9-pyrazoloanthrone (IV), gave a yellow solution in acetone which slowly became dull red after solid potassium hydroxide had been added, resembling *meso*benzanthrone which affords a deep green solution in similar circumstances (B.P. 319,593; 322,253).

* Part I, preceding paper.

The *N*-methyl derivative, m. p. 229° (VII), was much more reactive towards amines, alkalis in the presence of oxidants, and acetone containing an alkali hydroxide. With sodium anilide substitution was not observed but, instead, mainly coupling of two molecules occurred, to form (VIII). An acetone solution of (VII), to which solid potassium hydroxide was added, rapidly became red, and then, through violet, blue. The blue colour was probably that of (IX). The reaction occurred much more readily than with (IV).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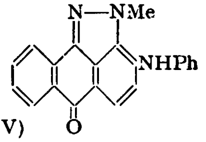
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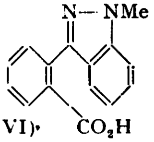
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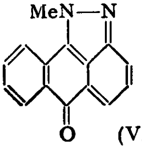
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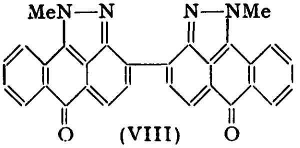
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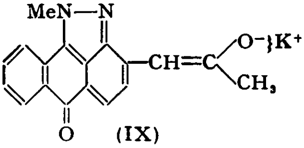
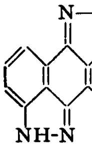
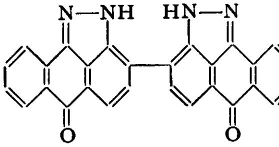

(IX)

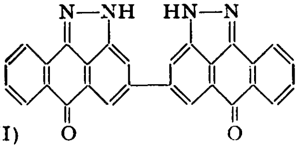
1 : 9-5 : 10-Dipyrazoloanthracene * (X) (Mohlau, *Ber.*, 1912, **45**, 2244) does not react with sodium anilide, and is recovered unaltered after fusion with potassium hydroxide and manganese dioxide.


(X)


(XI)

The properties of (X) show clearly how essential is the carbonyl group for the reactivity of pyrazoloanthrone and its *N*-methyl derivatives towards bases. The derivative (VII) is much more reactive than (V), probably because in (VII) the nucleus carrying the carbon atoms 2, 3, and 4 approaches more closely a typical open-chain aliphatic αβ-unsaturated ketone in the degree of its unsaturation.

Conversion of 1 : 9-pyrazoloanthrone into a yellow colouring matter by hot alcoholic potassium hydroxide was first described in G.P. 255,641. Conversion of the product into a potassium salt and alkyl derivatives followed G.P. 301,554, 302,259, 302,260). Mayer and Heil first (*Ber.*, 1922, **55**, *B*, 2155) proposed a highly condensed structure but later (*Chem.-Ztg.*, *Fortschrittber.*, 1929, 56) showed that the product of the alkali fusion was di-(1 : 9-pyrazoloanthron-2-yl) (XI).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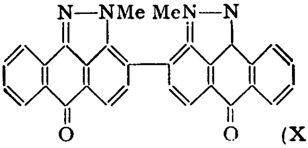

(XIII)

A more detailed study of the alkylation of (XI) (G.P. 301,554, 302,259, 302,260) has shown that mono- and di-alkyl derivatives can be prepared, and that the dialkyl compounds exist in two forms (G.P. 359,139, 463,246) : methylation is stated to yield an orange dimethyl derivative, m. p. 350°, soluble in chlorobenzene, and an insoluble red dimethyl derivative. The latter derivative differs also in separating from sulphuric acid as a sulphate. The red derivative results directly by the alkali fusion of one, and only one, of the *N*-methyl derivatives of 1 : 9-pyrazoloanthrone (G.P. 456,763, 479,284). Maki and Akamastsu (Ann. Meeting Soc. Chem. Ind. Japan, 1949; Rept. Jap. Assoc. Promotion

* For numbering see footnote, p. 1630.

Sci., 1949) prepared two monoethyl derivatives of 1 : 9-pyrazoloanthrone; one isomer, of m. p. 145°, yields a red colouring matter when it is fused with alkali, whilst the other, of m. p. 186·5°, remains unchanged. Maki and Akamastsu consider that steric factors determine the result and regard the *N*-ethyl compound, m. p. 145°, and the derived red colouring matter as the ethyl analogues of (VII) and (VIII) respectively. Structure (IV; Et in place of Me) then remains to represent the *N*-ethyl-1 : 9-pyrazoloanthrone, m. p. 186·4°. The authors also point out that in (VII) "partial valency exists in the 2-position," and that (VIII; Et in place of Me), which is insoluble in chlorobenzene, must represent the red, chlorobenzene-insoluble colouring matter obtained by the direct ethylation of (XI).

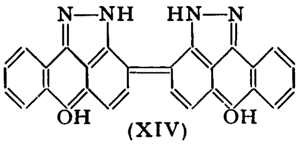
In the present experiments it was found that *N*-acetyl-2-bromo-1 : 9-pyrazoloanthrone gave (XI) directly when it was heated with copper in naphthalene, deacetylation having occurred in the reaction. The product was identical with the colouring matter obtained from 1 : 9-pyrazoloanthrone by alkali fusion as described in G.P. 255,641.

Attempts to prepare di-(1 : 9-pyrazoloanthron-3-yl) (XII) by the action of copper on *N*-acetyl-3-bromo-1 : 9-pyrazoloanthrone were unsuccessful; both deacetylation and debromination occurred.

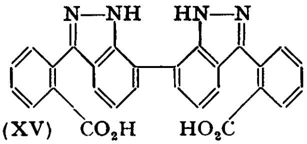
If heated with sodium anilide 1 : 9-pyrazoloanthrone afforded both (I) and (XI). Sodium *o*-toluidide gave both 2-*o*-toluidino-1 : 9-pyrazoloanthrone and (XI), but neither self-coupling nor nuclear substitution occurred when the condensing agent was sodium diphenylamide.

Sodium anilide and (IV) gave 2-anilino-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (V) and (XIII); the latter is a yellowish-orange colouring matter, m. p. 357°, identical in reactions with one of the *NN*′-dimethyl derivatives prepared by the methylation of (XI). Formation of (XIII) indicates that the presence of a methyl group near the 2-position of 1 : 9-pyrazoloanthrone does not inhibit self-condensation, and that the difference in behaviour of the two *N*-methyl derivatives of 1 : 9-pyrazoloanthrone is the result of a difference in their reactivity towards bases. If (XIII) is the constitution of the orange-yellow dimethyl derivative of pyrazoloanthrone-yellow (XI), the red derivative formed simultaneously during methylation with methyl sulphate and alkali is probably (VIII).

1 : 9-5 : 6-Dipyrazoloanthracene (X) was recovered unaltered after being heated with sodium anilide, ethyl alcoholic potassium hydroxide, or a mixture of manganese dioxide and potassium hydroxide.



(XIV)



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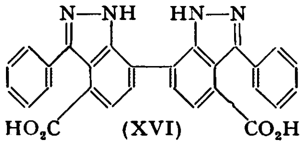
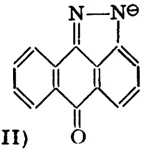


(XVI)

Although pyrazoloanthrone-yellow (XI) is structurally analogous to di*meso*benzanthron-4-yl there are important differences between them. Heating with alkaline dithionite leaves the di*meso*benzanthronyl almost unchanged whilst (XI) dissolves with a deep blue colour. The blue solution contains a salt of the dihydro-derivative (XIV) which is also formed when a suspension of (XI) in aqueous alcoholic sodium hydroxide combines with two atoms of hydrogen in the presence of Raney nickel; no further reduction occurs during longer contact. In contrast, 1 : 9-pyrazoloanthrone takes up one molecule of hydrogen more slowly, forming a greenish-yellow solution.

Fusion with alkali hydroxides transforms di*meso*benzanthron-4-yl into violanthrone (Lüttringhaus and Neresheimer, *loc. cit.*), but (XI) undergoes ring-fission with formation of an acid, $C_{28}H_{18}O_4N_4$. The acid regenerates (XI) when heated with sulphuric acid, and for this reason the constitution is probably (XV) or (XVI), the former being preferred for the reason given on p. 1636.

Mechanism of the Self-condensation of 1 : 9-*Pyrazoloanthrone*.—As with *meso*benzanthrone, the self-union of 1 : 9-pyrazoloanthrone requires the use of basic condensing agents, such as alcoholic potassium hydroxide (Bradley and Jadhav, *J.*, 1948, 1622). For this reason it is probable that the first step in the formation of (XI) is the generation of anions of the reactant, which then condense with undissociated molecules of the same.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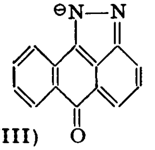
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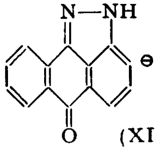
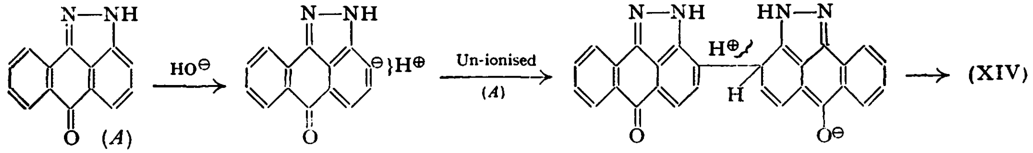

(XIX)

The structure of the anion is doubtless intermediate between (XVII), (XVIII), and (XIX), and the importance of the carbanion form may be gauged from the facts that alkylation of potassiopyrrole affords both *C*- and *N*-derivatives (Llubarvin, *Ber.*, 1869, **2**, 101; Bell, *ibid.*, 1878, **11**, 1810; Ciamician and Dennstedt, *ibid.*, 1882, **15**, 2581; Ciamician and Silber, *ibid.*, 1887, **20**, 1369; Ciamician and Zanetti, *ibid.*, 1889, **22**, 659; Zanetti, *ibid.*, p. 2518). Similarly, methyl iodide and the sodium derivative of indole afford 2- and 3- as well as 1-methylindole (Weissgerber, *ibid.*, 1910, **43**, 3521). The self-condensation of 1 : 9-pyrazoloanthrone may then be represented as in the annexed scheme.



That the free NH group of 1 : 9-pyrazoloanthrone is not essential for self-condensation is substantiated by the ready self-condensation of (VII) to (VIII), and by the successful, though less ready, condensation of (IV) to (XIII). In these two instances the basic condensing agent must bring about direct ionisation of nuclear hydrogen as envisaged with *meso*benzanthrone (Bradley and Jadhav, *loc. cit.*), and established by isotopic exchange in the case of *s*-trinitrobenzene (Kharasch, Brown, and McNab, *J. Org. Chem.*, 1937, **2**, 36).

The carbonyl group of 1 : 9-pyrazoloanthrone, however, is necessary for reaction; 1 : 9-5 : 10-dipyrazoloanthracene (X), which lacks a carbonyl group, does not undergo self-condensation in any circumstances.

The occurrence of self-union depends also on the condensing agent; the stronger the base the more facile is the reaction. 1′-Methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (IV), which is relatively inert, does not undergo self-condensation with alcoholic potassium hydroxide, but does so readily with sodium anilide. Sodium diphenylamide is unable to cause any of the compounds to condense.

Apart from the generation of anions, the self-condensation of 1 : 9-pyrazoloanthrone depends on the occurrence of αβ-unsaturated-ketone characteristics in the nucleus. In this connection the great activity of (VII) should be mentioned, contrasted with the relative inertness of (IV) in which there is no loss of aromatic character from bond-fixation.

A notable feature of the self-union of 1 : 9-pyrazoloanthrone and its *N*-methyl derivatives is the simultaneous formation of 2-anilino-derivatives. The latter result from substitution by anilide anions, and the occurrence of anion-substitution side-by-side with self-union supports the view that self-union, too, is an instance of anion-substitution, the substituting agent being the anion of 1 : 9-pyrazoloanthrone or one of its *N*-methyl derivatives.

A number of related matters may also be mentioned.

3-Bromo-1 : 9-pyrazoloanthrone, heated with alkalis, does not undergo coupling, but only replacement of bromine. The effect may be the result of steric hindrance, but a change in the electrical state of the 2-position resulting from the introduction of a bromine substituent is an equally probable explanation.

Lüttringhaus and Neresheimer (*loc. cit.*) observed that *meso*benzanthrone condensed readily with 3-chloro*meso*benzanthrone in the presence of sodium anilide to form 3 : 4′-di-*meso*benzanthronyl (cf. Bradley and Jadhav, *J.*, 1948, 1623). We have found that the same condensing agent and a mixture of 1 : 9-pyrazoloanthrone and its 2-bromo-derivative afford only 2-anilino-1 : 9-pyrazoloanthrone. Evidently in the 1 : 9-pyrazoloanthrone series the simple replacement of bromine by anilide anions occurs much more readily than the generation of 1 : 9-pyrazoloanthron-2-yl anions.

1 : 9-Pyrazoloanthrone and its derivatives differ from *meso*benzanthrone and violanthrone in undergoing hydrolysis with fused alkali hydroxides. The effect may be the result of the close relation of the 1 : 9-pyrazoloanthrones to amides, of which they may be regarded as vinylogues (cf. Fuson, *Chem. Reviews*, 1935, **16**, 1; Bradley, *J.*, 1949, 2712). The amide relationship supports the constitutions (II, VI, XV) proposed for the acid products of hydrolysis.

EXPERIMENTAL

Di-(1 : 9-*Pyrazoloanthron-2-yl*).—(*a*) 1 : 9-Pyrazoloanthrone (15 g.), heated with ethyl-alcoholic potassium hydroxide (Mayer and Heil, *Ber.*, 1922, **55**, *B*, 2155), afforded a product (14·5 g.) which, after extraction with acetone, yielded an insoluble residue of di-(1 : 9-pyrazoloanthron-2-yl) (12·5 g.).

(*b*) *N*-Acetyl-2-bromo-1 : 9-pyrazoloanthrone (1 g.) was heated with copper bronze (1 g.) in naphthalene (1 g.) at 250° for 9 hours (G.P. 457,182). The naphthalene was then distilled in steam, and the copper salts and unreacted copper were dissolved in a mixture of ammonia and ammonium chloride. The brown residue (0·5 g.) was extracted with boiling chlorobenzene (2 × 300 c.c.), and the undissolved material (0·3 g.) further extracted with hot pyridine (100 c.c.). The resulting solution, treated with charcoal and filtered, afforded a brown solid (0·1 g.), m. p. >360° (Found: N, 12·6; Ac, 0. Calc. for $C_{28}H_{14}O_2N_4$: N, 12·7%). This gave all the reactions of di-(1 : 9-pyrazoloanthron-2-yl) prepared as in (*a*). Also, like this compound, it dissolved in pyridine with a yellow colour, changed to violet on the addition of methanolic potassium hydroxide.

(*c*) Aniline ("AnalaR"; 60 g.) was heated under reflux. Sodium (2·4 g.), copper bronze (0·1 g.), and nickel oxide (0·1 g.) were added in succession, and the mixture was stirred until hydrogen ceased to be evolved. The temperature was then kept at 40—45° while 1 : 9-pyrazoloanthrone (9 g.) was added, and subsequently raised to 45—60° for 30 minutes. Aniline (30 g.) was added to the viscous product and the stirring continued for 2 hours. After cooling, and addition to dilute hydrochloric acid, the precipitated yellow solid (10 g.) was collected, washed, and dried. Extraction with acetone (Soxhlet) afforded an insoluble residue (5·9 g.) and a solution. The residue was identical with the di-(1 : 9-pyrazoleanthron-2-yl) prepared as in (*a*). The acetone solution afforded brownish-yellow crystals, m. p. 357° (Found: N, 13·2. $C_{20}H_{13}ON_3$ requires N, 13·5%), identical in reactions with the 2-anilino-1 : 9-pyrazoloanthrone prepared from 2-bromo-1 : 9-pyrazoloanthrone and sodium anilide. It dissolved in concentrated sulphuric acid forming a wine-red solution having a faint green fluorescence. Its solution in pyridine was yellow and showed a green fluorescence; on the addition of methanolic potassium hydroxide a wine-red colour and a bright yellow fluorescence developed. It dissolved in 20% aqueous sodium hydroxide forming an orange solution having a green fluorescence; on the addition of sodium dithionite a pale yellow solution and a weak bluish-green fluorescence resulted.

2-*Anilino*-1 : 9-*pyrazoloanthrone*.—A solution of sodium anilide in aniline was prepared from aniline (60 c.c.) as described in (*c*) (above). 2-Bromo-1 : 9-pyrazoloanthrone (4 g.) was added, and the mixture was stirred at 60° for 3 hours. It was then added to dilute hydrochloric acid. The yellowish-brown precipitate was collected, washed, and dried (4 g.; m. p. 324—330°). Recrystallisation from chlorobenzene gave yellowish-brown needles, m. p. 351—352°, not depressed on mixing with the compound, obtained as above.

Action of Copper on N-*Acetyl*-3-*bromo*-1 : 9-*pyrazoloanthrone*.—*N*-Acetyl-3-bromo-1 : 9-pyrazoloanthrone (2 g.), copper bronze (2 g.), and naphthalene (2 g.) at 250° (8 hours) afforded a product from which naphthalene, copper salts, and unchanged copper were then removed. The residue, extracted with alcohol, afforded a product (0·3 g.), m. p. 241—242° (Found: N, 9·9; Br, 2·8%), mainly 1 : 9-pyrazoloanthrone. Further extraction with chlorobenzene also afforded 1 : 9-pyrazoloanthrone, and, finally, extraction with pyridine dissolved a product, m. p. 252—256° (Found: N, 9·6; Br, 16·0%), consisting essentially of 3-bromo-1 : 9-pyrazoloanthrone. There was no evidence for the formation of di-(1 : 9-pyrazoloanthron-3-yl).

A similar result was obtained when anthracene (1 g.) was used instead of naphthalene and the reaction was carried out at 250° for 12 hours.

1 : 9-5 : 10-*Dipyrazoloanthracene*.—This compound (Found: N, 24·3. Calc. for $C_{14}H_8N_4$:

N, 24·6%) resulted in one stage when 1 : 5-dichloroanthraquinone was heated with pyridine and hydrazine hydrate as described by Mohlau (*loc. cit.*). The intermediate 1 : 5-dihydrazinoanthraquinone was not obtained.

1 : 5-Dichloroanthraquinone (10 g.), hydrazine hydrate (10 g.), sodium acetate (10 g.), and pyridine (130 c.c.) gave, after 5 hours at the b. p., 5-chloro-1 : 9-pyrazoloanthrone (m. p. 296—297°; 6 g.) and chlorobenzene-insoluble 1 : 9-5 : 10-dipyrazoloanthracene.

1 : 9-5 : 10-Dipyrazoloanthracene was recovered unaltered after being heated with an excess of a suspension of potassium hydroxide (2·8 g.) in alcohol (2 g.) (6 hours), sodium anilide (4 hours at 40—60°), or precipitated manganese dioxide (1·3 g.), potassium hydroxide (13 g.), and anhydrous potassium acetate (1·3 g.) (30 minutes at 200—250°).

NN-*Diacetyl*-1 : 9-5 : 10-*dipyrazoloanthracene*.—Finely ground 1 : 9-5 : 10-dipyrazoloanthracene dissolved slowly in hot acetic anhydride, forming a blue fluorescent solution. Soon golden-yellow needles began to separate and the fluorescence became yellow. The *diacetyl* derivative which separated from the hot, filtered solution had m. p. 334° [Found : N, 17·7; Ac, 29·4. $C_{14}H_6N_2(O{\cdot}CO{\cdot}CH_3)_2$ requires N, 18·0; Ac, 28·0%].

Dimethyl Derivatives of Di-(1 : 9-*pyrazoloanthron*-2-*yl*).—(*a*) A solution of di-(1 : 9-pyrazoloanthron-2-yl) (4 g.) in water (100 c.c.) and alcohol (100 c.c.) containing sodium hydroxide (10 g.) was stirred at 30—40° while methyl sulphate (10 g.) was added. After 6 hours the product was cooled and set aside for 12 hours, and the precipitated solid collected. This was extracted with ethyl-alcoholic potassium hydroxide, and the residue (2·6 g.) was extracted further with acetone (Soxhlet). A yellow solid, m. p. 336—337°, dissolved, and this was sublimed *in vacuo*. The purified dimethyl derivative (XIII) had m. p. 349° (Found : N, 12·2. Calc. for $C_{30}H_{18}O_2N_4$: N, 12·0%). It dissolved in concentrated sulphuric acid with a reddish-orange colour, and in alkaline sodium dithionite with a bluish-green colour; the original yellow compound separated when the solution was exposed to air.

The acetone-insoluble portion (0·9 g.) of the methylation product did not melt below 360°. It was identical in reactions with the compound formed by the action of ethyl-alcoholic potassium hydroxide on 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone.

(*b*) 1′-Methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (3 g.) was stirred for 3 hours at 40—60° with sodium anilide prepared from sodium (1 g.) and aniline (25 g.). The product was cooled and added to dilute hydrochloric acid, and the precipitate collected, washed, and dried. On extraction with acetone deeply coloured solutions formed at first, but later a product dissolved more sparingly and with a pale yellow colour. This was collected separately and isolated in the form of small yellow crystals, m. p. 356—358° (Found : C, 76·6; H, 4·1; N, 11·9. Calc. for $C_{30}H_{18}O_2N_4$: C, 76·9; H, 3·9; N, 12·0%), identical in reactions with the acetone-soluble dimethyl derivative recorded in (*a*).

The deeply coloured acetone extracts formed initially yielded 1·75 g. of a brown solid, m. p. 116—121°, on evaporation. This was dissolved in benzene and chromatographed on alumina. A weakly adsorbed band formed consisting of unchanged 1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)-anthrone, but there was also a more strongly adsorbed reddish band. The red product eluted with acetone gave a green-fluorescent yellow solution from which was isolated a yellow compound, m. p. 184—186° (Found : C, 77·4; H, 4·8; N, 12·9. $C_{21}H_{15}ON_3$ requires C, 77·5; H, 4·6; N, 12·9%). It dissolved in concentrated sulphuric acid with a wine-red colour. A red colour developed on addition of methanolic potassium hydroxide to its solution in acetone. The strong colour reaction with alkali indicates that the compound, m. p. 184—186°, is 2-*anilino*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*. It should be noted also that 4-anilino-1 : 9-pyrazoloanthrone shows only a slight colour change (yellow-orange) when alkali is added to its solution in pyridine (Part I, p. 1634).

(*c*) 1′-Methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (3 g.) was stirred for 3 hours at 50—60° with sodium anilide prepared from sodium (1 g.) and aniline (30 g.). Even after 10 minutes the colour had changed to deep bluish-green. The product was added to dilute hydrochloric acid, and the brown precipitate collected, dried, and extracted with acetone. A portion dissolved leaving a brown residue (2 g.) of *dimethyl* derivative (VIII), m. p. >360°, unaltered on crystallisation from chlorobenzene (Found : C, 77·2; H, 4·3; N, 12·5%). It dissolved in chlorobenzene to a bluish-red solution, and in alkaline sodium dithionite with a blue colour; aëration of the blue solution afforded a red precipitate.

(*d*) 1′-Methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (2 g.), heated under reflux with potassium hydroxide (10 g.) and ethyl alcohol (25 c.c.) as described in G.P. 479,284, afforded a product which was then extracted with acetone and chlorobenzene in succession. The reddish-brown residue (0·7 g.) of dimethyl derivative had m. p. >360° (cf. above) (Found : N, 12·1%).

(*e*) 2-Bromo-1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (0·5 g.) was stirred with a solution of sodium dithionite (1 g.) and potassium hydroxide (1 g.) in water (20 c.c.) at 60—80° for 15 minutes. The colour changed gradually from yellow through green to blue. Water was then added, the solution aërated, and the resulting precipitate collected. Extraction with acetone afforded a residue (0·2 g.) having the properties of di-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl].

Action of Potassium Hydroxide and Manganese Dioxide on 1 : 9-*Pyrazoloanthrone. Formation of* 3-o-*Carboxyphenylindazole.*—An intimate mixture of 1 : 9-pyrazoloanthrone (10 g.) and precipitated manganese dioxide (10 g.) was added during 15 minutes to a stirred melt of potassium hydroxide (75 g.) and potassium acetate (7·5 g.) at 200—220°. As the reaction progressed the melt thickened and it was necessary to raise the temperature to 250°. After 30 minutes at 220—250° the product was added to water (1·5 l.), and the suspension was heated for some time at 60° and then filtered. There was a considerable residue, and a deep yellow filtrate which exhibited a green fluorescence. Acidification of the filtrate gave a yellow precipitate, and this was collected, washed, dried (5·6 g.; m. p. 184—186°), and extracted with benzene (Soxhlet). The benzene extract afforded brown crystals (A) (3·6 g.), m. p. 235—246°. Evaporation of the mother-liquor gave 0·8 g. of *acid* which, sublimed *in vacuo*, was obtained as colourless crystals, m. p. 237—238° (Found : C, 69·7; H, 4·6; N, 12·1. $C_{14}H_{10}O_2N_2$ requires C, 70·5; H, 4·2; N, 11·8%), and showed the same reactions as (A). It dissolved in sodium hydrogen carbonate solution with evolution of carbon dioxide. It gave a yellow solution, having a green fluorescence, in concentrated sulphuric acid, and in acetone to a yellow solution which exhibited a blue fluorescence, changed on the addition of potassium hydroxide to a yellow solution with a yellow-green fluorescence.

The acid (A) (0·9 g.) was heated in concentrated sulphuric acid (15 c.c.) at 95—100° for an hour. On addition to water a pale brown precipitate formed. This, collected, washed, and dried, had m. p. 283° and did not depress the m. p. of 1 : 9-pyrazoloanthrone.

The benzene-insoluble portion of the original reaction product was also an acid (0·8 g.). It dissolved in aqueous sodium hydrogen carbonate, and gave a yellow solution in acetone which exhibited a greenish-blue fluorescence; on addition of methyl-alcoholic potassium hydroxide the acetone solution became brownish-yellow and developed a greenish-yellow fluorescence.

Heating (A) with acetic anhydride afforded an *acetyl* derivative, m. p. 217—218° after softening at 189° (Found : C, 68·2; H, 4·4; N, 10·2. $C_{16}H_{12}O_3N_2$ requires C, 68·5; H, 4·3; N, 10·0%).

Action of Potassium Hydroxide and Manganese Dioxide on 1′-*Methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone. Formation of* 3-o-*Carboxyphenyl*-1-*methylindazole.*—1′-Methylpyrazolo-(5′ : 4′ : 3′-1 : 13 : 9)anthrone (10 g.) and manganese dioxide (10 g.) were heated with potassium hydroxide (50 g.) and potassium acetate (5 g.) for 10 minutes at 200°, and then for 20 minutes at 220—230°. The alkaline solution obtained on addition to water was filtered and acidified; it afforded 8·4 g. of an *acid*, m. p. 190—194°. Extraction with benzene gave 7·0 g. of brownish-yellow crystals, m. p. 205—206° (Found : N, 11·0. $C_{15}H_{12}O_2N_2$ requires N, 11·1%). There was a considerable residue (B).

The compound, m. p. 205—206°, was easily soluble in aqueous sodium hydrogen carbonate with evolution of carbon dioxide and formation of a yellow solution having a greenish-yellow fluorescence. It gave a yellow solution having a blue fluorescence in acetone, changed to yellow with a yellow-green fluorescence on addition of methanolic potassium hydroxide. It was unchanged by hot acetic anhydride. It depressed the m. p. of 4-hydroxy-1′-methylpyrazolo-(5′ : 4′ : 3′-1 : 13 : 9)anthrone, m. p. 204—205°. When heated with 10 c.c. of concentrated sulphuric acid at 95—100° for an hour 0·7 g. of the acid yielded 0·6 g. of a bright yellow derivative, m. p. 174°. Crystallisation from benzene gave the product in the form of yellow needles, m. p. 185°, shown by colour reactions and mixed m. p. to be 1′-methylpyrazolo-(5′ : 4′ : 3′-1 : 13 : 9)anthrone.

The benzene-insoluble portion (B) of the oxidation product was also an acid (0·85 g.). It did not melt below 360°. It dissolved in aqueous potassium hydrogen carbonate, forming a pale yellow solution with a blue fluorescence. In aqueous potassium hydroxide the solution was yellow with a bright yellowish-green fluorescence.

Action of Fused Potassium Hydroxide on Di-(1 : 9-*pyrazoloanthron*-2-*yl*).—Di-(1 : 9-pyrazoloanthron-2-yl) (3 g.) was stirred for an hour at 220—250° with potassium hydroxide (30 g.) and potassium acetate (3 g.). The product was added to water, and the suspension was heated and filtered. A yellow filtrate having a green fluorescence was obtained, and this on acidification afforded a gelatinous, brown precipitate. After being washed and dried, the precipitate (1·85 g.)

was extracted with acetone. Evaporation of the extract gave cream-coloured *di-*(3-o-*carboxyphenylindazolin-*7*-yl*) (0·6 g.), m. p. 330—331° (Found: N, 11·5. $C_{28}H_{16}O_4N_4$ requires N, 11·8%). This compound dissolved in aqueous potassium hydrogen carbonate with evolution of carbon dioxide and formation of a yellow solution having a blue fluorescence. A similar solution was obtained in acetone; on addition of methanolic potassium hydroxide the fluorescence became bright yellowish-green. Heating with concentrated sulphuric acid at 90° for an hour reconverted the acid, m. p. 330—331°, into di-(1 : 9-pyrazoloanthron-2-yl).

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