1 : 9-*Pyrazoloanthrone. Part III.* The Chemistry of the Two* N-*Methyl Derivatives of* 1 : 9-*Pyrazoloanthrone.*

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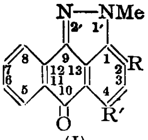
The properties of the two *N*-methyl derivatives of 1 : 9-pyrazoloanthrone have been studied in continuation of previous work (*J.*, 1952, 1636). 1′-Methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (I) resembles *meso*-benzanthrone in that electron-donating agents cause nuclear substitution with or without self-union of (I). With the same reagents 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (II) undergoes self-union almost exclusively. Several derivatives of (I) and (II) are described.

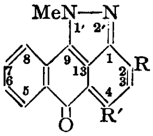
Bradley and Geddes (*J.*, 1952, 1636) showed that the two *N*-methyl derivatives (I, II; R = R′ = H) of 1 : 9-pyrazoloanthrone had widely different properties, and attributed the fact to the presence of an *o*-quinonoid nucleus in (II), a consequence of bond-fixation. The two isomers and their derivatives have now been further studied in order to determine the extent of the bond-fixation effect.

Bradley and Geddes showed that heating with piperidine caused replacement of the halogen in the 2-bromo-, 4-chloro-, and 5-chloro-derivatives of 1 : 9-pyrazoloanthrone, whilst 3-bromo- and 8-chloro-derivatives were inert, and further, that the 4-bromo-derivative (I; R = H, R′ = Br) gave 4-hydroxy-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)-anthrone (I; R = H, R′ = OH) on being heated with methanolic sodium methoxide. In the present experiments the 2-bromo-, 3-bromo-, 4-bromo-, 5-chloro-, and 8-chloro-derivatives (I) have been prepared and their reactions with piperidine, morpholine, aniline, and, in two cases, with sodium methoxide have been studied. Replacement of halogen occurred readily when it occupied position 2, 4, or 5, but in the 3- or 8-position it was inert. The 2-bromo-, 5-chloro-, and 8-chloro-derivatives (II) were also prepared and it was found that the halogen of the 2-bromo-derivative was easily replaced by piperidine and morpholine, and that of the 5-chloro-compound by morpholine, whilst the 8-chloro-substituent was inert. The results indicate a marked similarity in properties of corresponding halogen derivatives whether they are derived from 1 : 9-pyrazoloanthrone or either of its *N*-methyl derivatives.

The halogen derivatives of (I) were prepared from methylhydrazine and (*a*) 1 : 2-dibromoanthraquinone (for the 2-bromo-derivative), (*b*) 1 : 3-dibromoanthraquinone (for the 3-bromo-derivative), (*c*) 1 : 5-dichloroanthraquinone (for the 5-chloro-derivative), and (*d*) 1 : 8-dichloroanthraquinone (for the 8-chloro-derivative). The halogen derivatives of (II) were prepared by the methylation of the corresponding derivatives of 1 : 9-pyrazoloanthrone (Bradley and Geddes, *loc. cit.*) by methanol and sulphuric acid.



(I)



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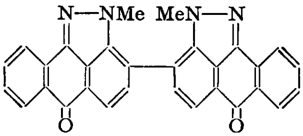

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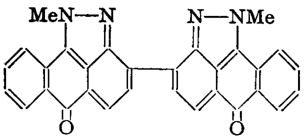

(IV)

1 : 9-Pyrazoloanthrone and its two *N*-methyl derivatives behave differently, however, in substitution reactions involving amines and similar reagents. These reactions are accompanied by the self-union of 1 : 9-pyrazoloanthrone and its derivatives, di-[1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthron-2-yl] (III) being formed from (I), and di-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl] (IV) from (II).

On being heated with piperidine in the presence of sodamide (I; R = R′ = H) gave (III) as the main product, 1′-methyl-2-piperidinopyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (I; R = NC_5H_{10}, R′ = H) being formed in small yield. Similarly with morpholine–sodamide the main product was (III), the 2-morpholino-compound (I; R = NC_4H_8O,

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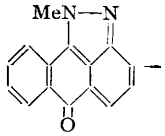
* Part II, *J.*, 1952, 1636.

R′ = H) resulting in small amount. The piperidino- and morpholino-derivatives were identical with the two compounds prepared by heating the corresponding 2-bromo-derivatives with piperidine and morpholine, respectively. Sodioaniline in aniline gave (III) and an anilino-derivative of (I) in approximately equal amounts. The anilino-derivative was not identical with 4- or 5-anilino-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)-anthrone. In all probability, like the morpholine and piperidine compounds, it was the 2-derivative. Methylmagnesium bromide and (I; R = R′ = H) gave 2 : 1′-dimethyl-pyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (I; R = Me, R′ = H), identical with the derivative prepared from 1-chloro-2-methylanthraquinone and methylhydrazine. Phenylmagnesium bromide gave a phenyl derivative of (I); the orientation was not established. Acetophenone and potassium hydroxide similarly converted (I; R = R′ = H) into the 2-methyl derivative (I; R = Me, R′ = H), the expected 2-phenacyl derivative (I; R = CH_2·COPh, R′ = H) being hydrolysed during the reaction. With potassium hydroxide in *tert.*-butyl alcohol the product was (III). This reaction did not occur when the medium was methyl, ethyl, or propyl alcohol; for this reason the self-union of (I) cannot involve reduction by the condensing agent. Fused potassium hydroxide caused hydroxylation and hydrolysis with opening of the ketone ring. Potassiocarbazole did not react, an indication that the nuclear reactivity of (I) towards this reagent is smaller than that of nitrobenzene (G. and M. de Montmollin, *Helv. Chim. Acta*, 1923, **6**, 94).

With piperidine and sodamide (II; R = R′ = H) gave (IV), together with a small amount of 1′-methyl-2-piperidino-pyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (II; R = NC_5H_{10}, R′ = H). Morpholine–sodamide similarly gave (IV) with a small amount of 1′-methyl-2-morpholinopyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (I; R = NC_4H_8O, R′ = H). The piperidino- and morpholino-compounds were identical with those prepared by heating the corresponding 2-bromo-derivative (II; R = Br, R′ = H) with piperidine and morpholine, respectively. Sodioaniline, methylmagnesium bromide, phenylmagnesium bromide, potassium hydroxide–acetophenone, -acetone, -acetonitrile, fused potassium hydroxide, potassium hydroxide in a range of boiling alcohols, and sodium methoxide in methanol all gave (IV) as the only product.

1′-Methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone resembles *meso*benzanthrone closely. Of the two, the latter is the more reactive as its conversion into 4 : 4′-di*meso*benzanthronyl by ethanolic potassium hydroxide at 110—120° shows. In agreement methylmagnesium iodide gives the 6-methyl derivative with *meso*benzanthrone and the 2-methyl derivative with 1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone, the substituent entering the nucleus nearer the carbonyl group in the more reactive compound (Bradley and Sutcliffe, *J.*, 1954, 708). As was stated by Bradley and Geddes (*loc. cit.*), (II; R = R′ = H) is more reactive than (I). Bases of widely different types, including the Grignard reagent, cause the self-union of (II) to (IV) unaccompanied by nuclear substitution by the reagent. The enhanced ease of self-union of (II) must be related to its *o*-quinonoid form. Yet it cannot arise simply in the marked unsaturation of *o*-quinonoid groups, for self-union is not a characteristic property of the most reactive αβ-unsaturated ketones. An alternative possibility is that the *o*-quinonoid grouping of (II) loses proton more readily than (I), the anion (V) being formed. Reaction of (V) with unchanged (II) then gives (IV) by the mechanism proposed by Bradley and Geddes.



(V)

EXPERIMENTAL

The 1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (I; R = R′ = H) used had m. p. 185—189° after recrystallisation from chlorobenzene, and m. p. 189° (Found: C, 77·1; H, 4·1; N, 11·9. Calc. for $C_{15}H_{10}ON_2$: C, 76·9; H, 4·2; N, 11·9%) after chromatography from benzene on alumina. 1′-Methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (II; R = R′ = H) had m. p. 229° (Found: C, 76·8; H, 4·3; N, 12·4%) after similar treatment.

Action of Reagents on (I; R = R′ = H).—(a) *Sodamide–piperidine.* Equimolar amounts of sodamide (1·9 g.) and the methyl-anthrone (11·7 g.) were refluxed in dry piperidine (50 c.c.) for 7 hr. The resulting viscous, black solution on addition to ice gave a green solution. This became reddish-brown on aeration and filtration gave a brown solid. On extraction with concentrated hydrochloric acid the solid afforded a deep brown solution. This was filtered off, then basified with ammonia, and the precipitated tar was collected, dried, and chromatographed in benzene on alumina. The main band was reddish-brown; it was eluted with acetone, and the extract evaporated. A small amount of reddish solid, m. p. 238—240°, was obtained which did not depress the m. p. of 1′-methyl-2-piperidinopyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone. The material remaining from the acid extraction (5 g.) was extracted with acetone (Soxhlet). In this way di-[1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthron-2-yl] (III) was obtained as an orange-yellow solid, m. p. 355—356° (Found: C, 77·0; H, 4·3; N, 11·6. Calc. for $C_{30}H_{18}O_2N_4$: C, 77·0; H, 3·9; N, 12·0%).

(b) *Sodamide–morpholine.* When heated under reflux in dry morpholine (50 c.c.) for 6 hr., sodamide (1·9 g.) and (I; R = R′ = H) (11·7 g.) gave a blackish-green solution, which on addition to water afforded a green solution. On aeration the colour was discharged and an orange brown solid was precipitated. Treated as in (*a*), the product gave 0·5 g. of an acid-soluble substance and a much larger amount of (III), m. p. 357—358° (Found: C, 76·9; H, 4·2; N, 11·9%). The basic substance after chromatography from benzene on alumina and elution with acetone gave 1′-methyl-2-morpholinopyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone, m. p. 215—217°, not depressed by the authentic compound (see below).

(c) *Sodioaniline.* A solution prepared from aniline (300 c.c.), sodium (5 g.), copper bronze (0·1 g.), and nickel oxide (0·1 g.) was refluxed for 2 hr. with 8 g. of (I; R = R′ = H). Treatment as in (a) gave 6 g. of a solid. This was extracted with cold acetone, and the dissolved material was recovered, dissolved in benzene, and chromatographed on alumina. The main red-brown band was eluted with acetone, and the product, m. p. 180—181°, was further purified by sublimation *in vacuo*. 2-*Anilino*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone* was obtained as bright orange crystals, m. p. 186° (Found: C, 77·65; H, 4·6; N, 12·4. $C_{21}H_{15}ON_3$ requires C, 77·45; H, 4·6; N, 12·9%) depressed to 161° on admixture with the 4-anilino-isomer. The material insoluble in cold acetone dissolved in the hot solvent. Evaporation gave (III), m. p. 354—356° (Found: C, 76·7; H, 4·0; N, 12·0. Calc. for $C_{30}H_{18}O_2N_4$: C, 77·0; H, 3·9; N, 12·0%).

(d) *Potassium hydroxide–acetophenone.* Potassium hydroxide (60 g.) and (I; R = R′ = H) (10 g.) were mixed intimately, added to dry pyridine (200 c.c.), and warmed to 50°. On the addition of acetophenone (30 c.c.) the colour became brown, then green, and after 5 hr. deep blue. After 12 hr. the resulting suspension was added to alcohol (400 c.c.) and then to ice; finally it was refluxed for 3 hr. The colour changed from blue to brown and a tar separated. This was collected when cold, and extracted with benzene, and the solution was chromatographed on alumina. Elution with benzene gave a sequence of tarry substances followed by a crystalline fraction, m. p. 210—215°. Sublimation *in vacuo* gave 1′ : 2-*dimethylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*, m. p. 216—218° (Found: C, 76·8; H, 4·9; N, 11·0. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·8; N, 11·2%), not depressed by the authentic compound prepared from 1-chloro-2-methylanthraquinone and methylhydrazine.

Acetone also reacted with (I; R = R′ = H) in the presence of potassium hydroxide but crystalline products could not be isolated.

(e) *Methylmagnesium bromide.* 1′-Methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (5 g.) was added in small successive amounts during 30 min., and with stirring, to a solution prepared from magnesium (12 g.), methyl bromide (50 g.), and ether (500 c.c.). The resulting red solution was refluxed for 3 hr., then added gradually to acetic acid (300 c.c. of 30%). After distillation in steam a tarry product separated from the remaining solution. It was collected, dried in air, then digested with benzene. The yellowish-brown residue (4 g.; m. p. 208—212°) crystallised from chlorobenzene as bright yellow needles, m. p. 220—221° (Found: C, 77·7; H, 4·9; N, 10·7. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·8; N, 11·2%), not depressed by authentic 1′ : 2-dimethylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone prepared by the following method:

Methylhydrazine sulphate (6 g.), 1-chloro-2-methylanthraquinone (10 g.), anhydrous potassium carbonate (10 g.), and pyridine (150 c.c.) were refluxed for 12 hr. From the cooled solution a bright yellow solid (10 g.) separated, and this crystallised from chlorobenzene as fine yellow needles, m. p. 217—218° (Found: C, 77·4; H, 4·6; N, 11·6%). 1′ : 2-Dimethylpyrazolo-(5′ : 4′ : 3′-1 : 13 : 9)anthrone was insoluble in aqueous sodium hydroxide, and it was reduced with difficulty with alkaline sodium dithionite. It gave an orange solution in concentrated sulphuric acid. The greenish-yellow solution in pyridine became yellow with a green fluorescence on the addition of methanolic potassium hydroxide.

(f) *Phenylmagnesium bromide.* In a similar experiment 10 g. of 1′-methylpyrazolo-(5′ : 4′ : 3′-1 : 13 : 9)anthrone and the Grignard reagent from magnesium (15 g.), bromobenzene

(70 g.), and ether (400 c.c.) gave 5 g. of material, m. p. 190°, and m. p. 240—244° after recrystallisation from benzene (Found : C, 80·6; H, 4·5; N, 9·2. $C_{21}H_{14}ON_2$ requires C, 81·3; H, 4·5; N, 9·0%). This 1′-*methyl*-x-*phenylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone* gave a deep violet solution in concentrated sulphuric acid. On the addition of water the solution became green. The yellow solution in pyridine changed to dark green on the addition of methanolic potassium hydroxide. In other respects the derivative resembled 1′ : 2-dimethylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone.

(g) *Potassium hydroxide.* 1′-Methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (3 g.) was stirred into a melt of potassium hydroxide (30 g.) and potassium acetate (5 g.) at 170°. The temperature was raised to 280—300° for 2 hr., then lowered. The resulting melt was added to water and boiled, and the brown solution was filtered and acidified. The brown precipitate (1·9 g.) was dissolved in sodium carbonate solution (charcoal), recovered by acidification, and extracted with acetone, and the soluble fraction (m. p. 200—204°) was crystallised from chlorobenzene. The pure 3-*o*-carboxyphenyl-1-methylindazole, m. p. 205° (Found : C, 71·1; H, 4·6; N, 11·5. Calc. for $C_{15}H_{12}O_2N_2$: C, 71·4; H, 4·7; N, 11·1%), was identical with the compound having the same m. p. prepared by Bradley and Geddes by the action of potassium hydroxide and manganese dioxide on (I; R = R′ = H). When 0·5 g. was heated with 20 c.c. of concentrated sulphuric acid at 100° for 1 hr. 1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone, m. p. 179—180°, resulted.

The portion of the hydrolysis product which did not dissolve in acetone gave a yellow solution and a blue fluorescence in aqueous potassium hydrogen carbonate. In aqueous potassium hydroxide the fluorescence was green.

(h) *Potassium hydroxide in* tert.-*butyl alcohol.* Potassium hydroxide (2 g.) and 0·5 g. of (I; R = R′ = H) were ground together and then refluxed with 20 c.c. of *tert.*-butyl alcohol. The solution, initially yellow-brown, changed to reddish-brown; after 4 hours' heating it was green. The cooled solution was added to water and aerated, and the yellow-brown precipitate was collected, washed, dried (m. p. 240°), and extracted (Soxhlet) with acetone. 1′-Methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone dissolved first, then the extract became pale yellow with a green fluorescence, and evaporation gave di-[1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthron-2-yl], m. p. 356—357° (Found : C, 76·5; H, 4·0; N, 12·3. Calc. for $C_{30}H_{18}O_2N_4$: C, 77·0; H, 3·9; N, 12·0%). This compound did not result when the proportion of potassium hydroxide employed was smaller, or when *tert.*-butanol was replaced by alcohol, ethylene glycol, diethylene glycol, 2-methoxyethanol, or diethylene glycol monoethyl ether. Refluxing 2 g. of (I; R = R′ = H) with 4 g. of sodium in 50 c.c. of methanol for 5 hr. gave only unchanged (I). Similarly, only unchanged reagents were recovered when (I; R = R′ = H) (4·7 g.), potassium hydroxide (2·5 g.), and 2-aminoanthraquinone (4·4 g.) were heated with dimethylaniline (100 c.c.) for 8 hr. at 110—120°, and when (I; R = R′ = H) (4·7 g.), potassium hydroxide (2·5 g.), and 2-aminoanthraquinone (4·4 g.) were heated with dimethylaniline (100 c.c.) for 8 hr. at 110—120°. When (I) (4·7 g.), potassium hydroxide (10 g.), and 2-aminoanthraquinone (4·4 g.) were heated at 160—180°, with the addition of sufficient potassium acetate to keep the melt mobile, unchanged reagents and indanthrone resulted.

Action of Reagents on (II; R = R′ = H).—(a) *Sodamide–morpholine.* Equimolar amounts of sodamide (1·9 g.), (II; R = R′ = H) (11·9 g.), and morpholine (50 c.c.) were refluxed for 7 hr. The dark, tarry product was added to ice, and the brown resinous solid which separated was collected, dried, and extracted with concentrated hydrochloric acid. The bases so separated were chromatographed from benzene on alumina. The least strongly adsorbed fraction contained unchanged (II), m. p. 220—222°. The most strongly adsorbed was orange. On elution it gave 1′-methyl-2-morpholinopyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone, m. p. 274—275°, not depressed by the authentic compound.

The acid-insoluble fraction was extracted with acetone. A soluble fraction consisting of (II; R = R′ = H) was obtained and reddish-brown insoluble material. This was purified by making it into a paste with pyridine, adding 20% sodium hydroxide, heating to 70° and finally adding sodium dithionite. A blue solution resulted. This was filtered, the filtrate was aerated, and the orange-brown precipitate was collected, digested with acetone and then crystallised (m. p. >360°) from a large volume of chlorobenzene (Found : C, 75·9; H, 3·9; N, 12·2. Calc. for $C_{30}H_{18}O_2N_4$: C, 77·0; H, 3·9; N, 12·0%). It was identical in properties with di-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl] (IV).

(b) *Sodamide–piperidine.* Experiment (a) was repeated with the substitution of piperidine for morpholine; a similar crude product resulted. The acid-soluble fraction gave a bright bluish-red band and a more mobile dark brown band when it was chromatographed from benzene on alumina. Elution with acetone afforded a solid, m. p. 110—120°, from the red band, and an orange solid, m. p. 220—224°, from the brown band. The second was not depressed by 1′-methyl-2-piperidinopyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone, m. p. 228°, prepared from piperidine and 2-bromo-1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone.

The acid-insoluble fraction was di-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl], m. p. >360° (Found : C, 76·7; H, 4·3; N, 11·9%).

(c) *Sodioaniline.* This reagent, prepared from sodium (10 g.), aniline (500 c.c.), copper bronze (0·1 g.), and nickel oxide (0·1 g.), reacted with (II; R = R′ = H) to give only di-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl]. No anilino-derivative of (II) could be found. In the following experiments an attempt was made to estimate the rate of the self-coupling reaction.

1′-Methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (10 g.) was dissolved in aniline (100 c.c.) and at a determined temperature the solution was added to a stirred solution of sodioaniline at the same temperature, prepared as above from sodium (10 g.). After an interval a measured volume was withdrawn, added to 10% hydrochloric acid, and kept for several hours. The resulting suspension was filtered, the solid was washed, then dried, and finally extracted with acetone. The Table shows the results obtained in four experiments.

Temp.	Volume withdrawn (V) (c.c.)	Time (min.)	Wt. of solid in volume (V)	
			Insol. in HCl (g.)	Insol. in HCl and insol. in acetone (g.)
186°	40	2	1·210	0·680
		5	1·520	0·670
		10	2·280	0·730
		15	1·300	0·690
		20	1·190	0·700
145	60	2	0·985	0·770
		6	0·935	0·815
		10	0·906	0·800
		15	1·190	0·830
		20	1·390	0·800
106	40	2	1·170	0·650
		3	1·130	0·560
		8	1·030	0·560
		13	1·210	0·540
		30	1·100	0·550
50	40	2	0·850	0·150
		5	0·915	0·290
		10	1·005	0·400
		15	0·955	0·450
		25	1·105	0·460

(d) *Potassium hydroxide and acetophenone.* Potassium hydroxide (60 g.) and 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (10 g.) were ground together, and dry pyridine (200 c.c.) was added, and finally acetophenone (20 c.c.). The mixture was stirred at 30—40° for 2 days during which the colour changed from yellow-brown, through green, to blue. After addition to alcohol (400 c.c.) the whole was poured on ice, and the resulting solution was boiled for 5 hr. The colour changed to brown; on cooling, a tar separated. This solidified when kept, and was then washed with dilute hydrochloric acid and finally extracted with acetone. The residue (4 g.; m. p. >350°) was di-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl] (Found : C, 76·7; H, 4·1; N, 12·3. Calc. for $C_{30}H_{18}O_2N_4$: C, 77·0; H, 3·9; N, 12·0%).

The same product was obtained when acetone or acetonitrile was used instead of acetophenone in the above experiment.

(e) *Methylmagnesium bromide.* 1′-Methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (10 g.) was added in portions to a stirred solution of the Grignard reagent prepared from methyl bromide (50 g.), magnesium (12 g.), and ether (500 c.c.). A green colour developed and this changed to blue when the solution was refluxed for 6 hr. After addition to dilute acetic acid (300 c.c. of 30%) the colour changed to yellow-orange. Steam distillation gave a residual brown tar, and this was collected, dried, and digested with cold benzene. The product (Found : C, 76·5; H, 3·9; N, 12·2%) showed the properties of di-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl].

A similar product (1 g.) (Found : N, 12·3%) was obtained when the Grignard reagent used in the above experiment was replaced with one prepared from bromobenzene (70 g.), magnesium (15 g.), and ether (400 c.c.).

(f) *Sodium methoxide.* 1′-Methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (2 g.) was refluxed for several days with a solution prepared from sodium (3 g.) and methanol (50 c.c.). The colour changed rapidly to reddish orange and after several days to deep brown. The product was di-[1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthron-2-yl] (Found : N, 12·2%).

The same product resulted when 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (2 g.) was stirred at 230—240° for 2 hr. with potassium hydroxide (10 g.), or when 1′-methylpyrazolo-(3′ : 4′ : 5′-1 : 13 : 9)anthrone (0·5 g.) was refluxed with potassium hydroxide (0·5 g.) in *tert.*-butyl alcohol (20 c.c.) for 1·5 hr. The same result was obtained when the solvent was ethyl alcohol, ethylene glycol, diethylene glycol, 2-methoxyethanol, or diethylene glycol monoethyl ether.

(g) *Other reagents.* There was no evidence of a reaction when 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (II) was treated under the following conditions : (i) Potassium carbazole (3·5 g.) was finely ground with 4 g. of (II) and heated in dimethylaniline (100 c.c.) at 120—130° for 9 hr. (ii) Potassium hydroxide (2·5 g.), 2-aminoanthraquinone (4·4 g.), and 4·7 g. of (II) were heated in dimethylaniline (150 c.c.) at 140—150° for 6 hr. In a somewhat similar experiment potassium hydroxide (10 g.) and potassium acetate (1 g.) were melted together, 2-aminoanthraquinone (4·4 g.) and (II) were added, and the whole was stirred for 3 hr. at 200° : the only product isolated was indanthrone.

Action of Potassium Hydroxide and Manganese Dioxide on 1′-*Methylpyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)*anthrone. Formation of a Hydroxy-derivative of* 3-o-*Carboxyphenyl*-2-*methylindazole*.—An intimate mixture of manganese dioxide (10 g.) and 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)-anthrone (10 g.) was stirred at 240—250° for 2·5 hr. with potassium hydroxide (50 g.) and potassium acetate (5 g.). The product was cooled, boiled with water (1 l.), and filtered, and the residue was further extracted with dilute potassium hydroxide. The combined filtrates were acidified and the brown precipitate was collected, dried (m. p. 235—240°), and extracted with acetone. The solution afforded a solid. This was purified by dissolution in aqueous sodium carbonate (charcoal), re-precipitation (3 g.; m. p. 240°), and crystallisation from acetone (m. p. 190—198°) (Found : C, 67·5; H, 4·7; N, 10·5. $C_{15}H_{12}O_3N_2$ requires C, 67·1; H, 4·4; N, 10·4%). This *monohydroxy*-derivative of 3-*o*-carboxyphenyl-2-methylindazole dissolved in potassium hydrogen carbonate solution with a yellow colour and a green fluorescence; in potassium hydroxide the fluorescence was blue.

Replacement of Halogens in Derivatives of (I) *and* (II). *Reactions of* 2-*Bromo*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—(a) *Morpholine.* On being refluxed with morpholine (25 c.c.) for 3 hr. 2-bromo-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (0·5 g.) afforded a reddish-orange solution which changed to brown. Addition to water gave a product which was then chromatographed from benzene on alumina. Three bands were formed. The lower yellow band, eluted with acetone, gave 1′-*methyl*-2-*morpholinopyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)-*anthrone*, m. p. 218° (Found : C, 71·1; H, 5·8; N, 13·1. $C_{19}H_{17}O_2N_3$ requires C, 71·4; H, 5·3; N, 13·1%).

(b) *Piperidine.* In a similar experiment in which piperidine (25 c.c.) was used for 7 hr. the product was chromatographed from chlorobenzene on alumina. Two bands formed. The lower, dark red band eluted with acetone gave 1′-*methyl*-2-*piperidinopyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*, m. p. 240° (Found : N, 13·3. $C_{20}H_{19}ON_3$ requires N, 13·2%). It dissolved in concentrated sulphuric acid with an orange colour. The reddish-orange solution in pyridine was unaffected by the addition of methanolic potassium hydroxide.

3-*Bromo*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—Prepared from 1 : 3-dibromoanthraquinone and methylhydrazine and crystallised from chlorobenzene this compound had m. p. 248—249° (Found : C, 58·4; H, 3·1; N, 9·0; Br, 25·7. Calc. for $C_{15}H_9ON_2Br$: C, 57·5; H, 2·8; N, 9·0; Br, 25·5%). Bradley and Geddes (*loc. cit.*) record m. p. 242—244°. It did not react with morpholine at the b. p.

Reactions of 4-*Bromo*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—This compound, m. p. 249—250° (Found: C, 57·1; H, 2·6; N, 9·1; Br, 25·5. Calc. for $C_{15}H_9ON_2Br$: C, 57·5; H, 2·8; N, 9·0; Br, 25·5%), was prepared by Bradley and Geddes's method (*loc. cit.*). (a) *Morpholine.* After refluxing for 5 hr. a solution of 4-bromo-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)-anthrone (1 g.) in morpholine (50 c.c.), initially orange, became red. Addition to water gave a solid from which after collection, washing, drying (1 g., m. p. 190—200°), and recrystallisation from chlorobenzene, 1′-*methyl*-4-*morpholinopyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone* was obtained as orange needles, m. p. 236° (Found : C, 71·1; H, 5·4; N, 13·1%). It gave a pale yellow solution in both concentrated sulphuric acid and alkaline sodium dithionite. (b) *Piperidine.* In a similar experiment with piperidine (50 c.c.) the yield of crude product was 1 g., and the m. p. was 185—195°. Crystallisation from chlorobenzene afforded 1′-*methyl*-4-*piperidino*-

pyrazolo(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*, m. p. 207—208° (Found: C, 75·9; H, 6·2; N, 12·9%). (c) *Sodioaniline*. 4-Bromo-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (3 g.) was heated at 60—80° for 4 hr. with a solution of sodioaniline prepared from sodium (1 g.), aniline (30 c.c.), dimethylaniline (30 c.c.), copper bronze (0·1 g.), and nickel oxide (0·1 g.). On addition of the mixture to dilute hydrochloric acid (200 c.c.) the product separated as a dark brown solid (2·8 g.). Extraction with benzene gave a soluble fraction, m. p. 180—200°, and this when chromatographed from benzene on alumina gave two bands. The more strongly adsorbed band was red, and this after elution with acetone gave 4-*anilino*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*, m. p. 210° (Found: C, 77·1; H, 4·3; N, 13·1%), as an orange brown solid.

4-*Chloro*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—Prepared by a slight modification of Bradley and Geddes's method (*loc. cit.*) 4-chloro-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)-anthrone was obtained as needles, m. p. 268° (Found: N, 10·2; Cl, 13·0. Calc. for $C_{15}H_9ON_2Cl$: N, 10·4; Cl, 13·2%). The same compound (m. p. 264°) was also obtained by methylation of 4-chloro-1 : 9-pyrazoloanthrone (6 g.) with methyl sulphate (17 g.), sodium hydroxide (7 g.), water (70 c.c.), and alcohol (30 c.c.), followed by chromatography (Found: C, 66·7; H, 3·0; N, 10·7; Cl, 13·6. Calc. for $C_{15}H_9ON_2Cl$: C, 67·0; H, 3·3; N, 10·4; Cl, 13·2%). It gave a bright red solution in concentrated sulphuric acid and when heated with morpholine, piperidine, and aniline it gave the same 4-morpholino-, 4-piperidino-, and 4-anilino-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone as had been prepared from the 4-bromo-compound.

5-*Chloro*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—Prepared by refluxing 1 : 5-dichloroanthraquinone (30 g.), methylhydrazine sulphate (20 g.), anhydrous potassium carbonate (30 g.), and pyridine (200 c.c.) for 12 hr. The solution, deep red initially, changed to yellowish-orange, and when it was cooled a solid separated (20 g.). This could not be obtained in a homogeneous form by crystallisation or chromatography. It was therefore heated for 12 hr. in pyridine (100 c.c.) with methylhydrazine sulphate (3 g.) and anhydrous potassium carbonate (5 g.). A solid, m. p. 320—330°, crystallised on cooling, and when the mother-liquor was added to water 5-*chloro*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone* separated. Crystallisation from chlorobenzene gave the pure derivative, m. p. 254° (Found: C, 66·4; H, 3·6; N, 10·5; Cl, 13·7. $C_{15}H_9ON_2Cl$ requires C, 67·0; H, 3·3; N, 10·4; Cl, 13·2%). It dissolved in concentrated sulphuric acid with a deep red colour.

Recrystallisation of the material, m. p. 320—330°, from chlorobenzene, gave *dimethyldipyrazoloanthracene* as fine needles, m. p. 340—344° (Found: C, 73·4; H, 4·5; N, 21·2. $C_{16}H_{12}N_4$ requires C, 73·8; H, 4·6; N, 21·4%).

Reactions. (*a*) Morpholine. When refluxed with morpholine (25 c.c.) for 3·5 hr. 5-chloro-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (1 g.) gave a product which was purified by chromatography from chlorobenzene on alumina. The resulting 1′-*methyl*-5-*morpholinopyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone* formed orange crystals, m. p. 198—199° (Found: C, 71·2; H, 5·3; N, 13·2%). It dissolved in pyridine with a deep orange colour, but in concentrated sulphuric acid the solution was yellow. (*b*) Piperidine. In a similar experiment in which piperidine (25 c.c.) was used, the resulting orange needles of 1′-*methyl*-5-*piperidinopyrazolo*-(5′ : 4′ : 3′-1 : 13 : 9)*anthrone* had m. p. 210° (Found: C, 75·3; H, 5·9; N, 13·0%). This gave a deep red solution in pyridine and a yellow solution in concentrated sulphuric acid. (*c*) Aniline. When 5-chloro-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (1 g.) was refluxed with aniline (50 c.c.) for 20 hr. a reddish-brown solid separated on cooling, and chromatography from benzene on alumina gave 5-*anilino*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone* as red crystals, m. p. 174—176° (Found: C, 77·2; H, 4·8; N, 12·8%). The 5-anilino-derivative dissolved in pyridine with a red colour, but in concentrated sulphuric acid it formed a yellow solution. An additional amount of less pure material was obtained by addition of original mother-liquor to dilute hydrochloric acid.

8-*Chloro*-1′-*methylpyrazolo*(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—1 : 8-Dichloroanthraquinone (50 g.), methylhydrazine sulphate (30 g.), and dry potassium carbonate (45 g.) were refluxed for 12 hr. in pyridine (300 c.c.). The initial colour was deep reddish-orange but this became yellower at the end of the reaction and a solid (50 g.) separated on cooling. Recrystallisation of this *product* from chlorobenzene afforded yellow needles, m. p. 232—233° (Found: C, 66·8; H, 3·3; N, 10·0; Cl, 13·3%). It dissolved in pyridine with a golden-yellow colour and in concentrated sulphuric acid it formed an orange-red solution.

Reactions. There was no evidence of reaction when 8-chloro-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (1 g.) was refluxed for 7 hr. with morpholine (50 c.c.), for 20 hr. with aniline (50 c.c.), or for 6 hr. with a solution prepared from sodium (2·5 g.) and dry methanol (25 c.c.).

Dibromo-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)*anthrone*.—1′-Methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone (5 g.) was refluxed in glacial acetic acid (50 c.c.) while a solution of bromine (30 g.) in the same solvent (20 c.c.) was added gradually. Hydrogen bromide was liberated. On being cooled the solution afforded a bright yellow solid, and this was collected, washed, dried (3 g., m. p. 190—200°), and recrystallised several times from glacial acetic acid. The resulting *dibromo*-derivative, m. p. 289° (Found : C, 45·7; H, 1·9; N, 7·1; Br, 39·6. $C_{15}H_8ON_2Br_2$ requires C, 45·9; H, 2·0; N, 7·1; Br, 40·8%), dissolved in concentrated sulphuric acid with a deep red colour, and in pyridine to form a greenish-yellow solution which changed to orange on the addition of a drop of methanolic potassium hydroxide.

Reactions. (*a*) Morpholine. The dibromo-derivative (1 g.) was refluxed for 4·5 hr. with morpholine (50 c.c.). The solution, initially yellowish-orange, became deep reddish-orange, and on being cooled a solid separated. Crystallisation from chlorobenzene gave orange needles, m. p. 282—283° (Found : C, 57·3; H, 4·1; N, 10·4; Br, 19·9. $C_{19}H_{16}O_2N_3Br$ requires C, 57·2; H, 4·0; N, 10·5; Br, 20·1%). This *bromo-morpholino*-derivative formed a yellowish-orange solution in pyridine and a deep reddish-orange solution in concentrated sulphuric acid. (*b*) Piperidine. In a similar experiment with piperidine (50 c.c.), the product (1 g.) crystallised from chlorobenzene as orange needles, m. p. 228° (Found : C, 60·8; H, 4·8; N, 10·8; Br, 21·0. $C_{20}H_{18}ON_3Br$ requires C, 60·9; H, 4·5; N, 10·6; Br, 20·2%). This *bromo-piperidino*-derivative gave an orange solution in pyridine and a pale yellow solution in concentrated sulphuric acid. (*c*) Aniline. The dibromo-derivative (1 g.) was refluxed for 6 hr. with aniline (75 c.c.). After several days the solution afforded a deep red solid. This was collected, washed with hydrochloric acid, then water, and finally dried (m. p. 223—227°), and chromatographed from benzene on alumina. A single red zone was formed. Elution with acetone gave an *anilino-bromo*-derivative, m. p. 226° (Found : C, 61·9; H, 3·1; N, 10·3; Br, 20·5. $C_{21}H_{14}ON_3Br$ requires C, 62·3; H, 3·4; N, 10·3; Br, 19·8%). It dissolved in concentrated sulphuric acid with a deep red colour. It gave a pale orange solution in pyridine, changed to deep red (violet fluorescence) on the addition of methanolic potassium hydroxide.

2-*Bromo-1′-methylpyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)*anthrone*.—This compound was prepared by methylating 2-bromo-1 : 9-pyrazoloanthrone, and by brominating 1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone; it had m. p. 234° (Bradley and Geddes, *loc. cit.*, state m. p. 232—234°) (Found : C, 57·4; 57·6; H, 2·8, 3·2; N, 8·9, 8·7; Br, 25·5, 25·5. Calc. for $C_{15}H_9ON_2Br$: C, 57·5; H, 2·8; N, 9·0; Br, 25·5%).

Reactions. (*a*) Morpholine. On being refluxed for 5 hr. with morpholine (50 c.c.), 2-bromo-1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (1 g.) afforded a yellow solid, m. p. 270—275°, raised to 279° (Found : C, 70·8; H, 5·3; N, 13·3. $C_{19}H_{17}O_2N_3$ requires C, 71·4; H, 5·3; N, 13·1%) on recrystallisation from benzene. 1′-*Methyl-2-morpholinopyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)-*anthrone* affords an orange solution in concentrated sulphuric acid and a bright yellow solution with a green fluorescence in benzene or pyridine. (*b*) Piperidine. In a similar experiment with piperidine (50 c.c.) the crude product, m. p. 180—190°, was brownish-orange. It crystallised from chlorobenzene (green fluorescence) in glistening needles of 1′-*methy-2-piperidinolpyrazolo*-(3′ : 4′ : 5′-1 : 13 . 9)*anthrone*, m. p. 228° (Found : N, 13·3. $C_{20}H_{19}ON_3$ requires N, 13·2%). Its solutions in pyridine and concentrated sulphuric acid resembled those of the 2-morpholino-analogue.

5-*Chloro-1′-methylpyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)*anthrone*.—5-Chloro-1 : 9-pyrazoloanthrone was prepared by Bradley and Geddes's method (*loc. cit.*). The m. p. of the product after recrystallisation from chlorobenzene was 304° (Found : C, 65·9; H, 2·8; N, 11·1; Cl, 13·6. Calc. for $C_{14}H_7ON_2Cl$: C, 66·0; H, 2·7; N, 11·0; Cl, 13·9%). Methyl alcohol (120 c.c.) was added during 1·5 hr. to concentrated sulphuric acid (200 c.c.) which was cooled in ice-water and stirred. 5-Chloro-1 : 9-pyrazoloanthrone (60 g.) was added, and the temperature was raised to 180° and kept thereat for 4 hr. After being kept 12 hr. the solution was added to water and the greenish-brown precipitate was collected, washed with dilute alcoholic sodium hydroxide, and dried (55 g.). Recrystallisation from chlorobenzene gave material, m. p. 170—180°, and this was chromatographed from benzene on alumina. Two main bands resulted : (*a*) the yellow band on elution with acetone gave 5-chloro-1′-methylpyrazolo(5′ : 4′ : 3′-1 : 13 : 9)anthrone, m. p. 254° (Found : N, 10·3; Cl, 13·4%), not depressed by the authentic derivative prepared from 1 : 5-dichloroanthraquinone and methylhydrazine; (*b*) the orange band on elution with acetone gave 5-chloro-1′-methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone, m. p. 234° (Found : C, 66·7; H, 3·4; N, 10·2; Cl, 13·1%). It dissolved in pyridine with a greenish-yellow colour which was unaffected by the addition of methanolic potassium hydroxide.

Reaction with morpholine. On being refluxed with morpholine (50 c.c.) for 4 hr. 5-chloro-1′-

methylpyrazolo(3′ : 4′ : 5′-1 : 13 : 9)anthrone (1 g.) afforded a dark solution from which a deep red solid was precipitated on addition to water. Recrystallisation from chlorobenzene (m. p. 214—216°) followed by chromatography from benzene on alumina gave two bands. The lower, pale orange band was washed through the column and the remaining reddish-orange band was eluted with acetone. The extract gave *1′-methyl-5-morpholinopyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)-*anthrone*, m. p. 217—218° (Found: C, 71·2; H, 5·3; N, 12·9%). It dissolved in pyridine with a reddish-orange colour; in concentrated sulphuric acid it formed a pale yellow slution.

8-*Chloro*-1′-*methylpyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)*anthrone*.—Prepared by the action of hydrazine on 1 : 8-dichloroanthraquinone, 8-chloro-1 : 9-pyrazoloanthrone had m. p. 345° after crystallisation from chlorobenzene and sublimation (Found: C, 66·4; H, 2·8; N, 10·8; Cl, 13·4%). Mohlau (*Ber.*, 1912, **45**, 2244) records m. p. >360°. Bradley and Geddes (*loc. cit.*) give m. p. 246—247°. Methyl alcohol (180 c.c.) was added below 40° and with stirring to concentrated sulphuric acid (200 c.c.), and was followed by 8-chloro-1 : 9-pyrazoloanthrone (80 g.). The temperature was raised to 180° and kept thereat for 4 hr. The cooled solution was added to water and the greenish precipitate was collected, washed, and dried (72 g.). Extraction with benzene gave a soluble portion, m. p. 207—214°, and this was further purified by chromatography from benzene on alumina. The main band was orange; elution with alcohol gave 8-*chloro*-1′-*methylpyrazolo*(3′ : 4′ : 5′-1 : 13 : 9)*anthrone* as a yellow solid, m. p. 225° (Found: C, 67·1; H, 3·1; N, 10·3; Cl, 13·5%). The colour in concentrated sulphuric acid was reddish-orange. It dissolved in pyridine with a yellow colour unchanged on the addition of methanolic potassium hydroxide. The 8-chloro-derivative was recovered unchanged after 8 hours' refluxing with morpholine. Similar negative results were obtained when the reagent was piperidine, aniline, or methanolic sodium methoxide.

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