Vat Dyes of Pyrazoloanthrone Series. V. Self Condensation of 5-Chloropyrazoloanthrone

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Nuclear chloro derivatives of pyrazoloanthrone have been hitherto prepared from 1,x-dichloroanthraquinone and hydrazine hydrate in pyridine solution.[2] Recently Bradley and Geddes prepared 5-chloropyrazoloanthrone (III) also by this method from 1,5-dichloroanthraquinone,[3] but the obtained product had low and wide range of melting point (275–285°) and only after recrystallization melted at 298°. We have now synthesized 5-chloropyrazoloanthrone (III) from 1-amino-5-chloroanthraquinone (I) via potassium 5-chloroanthraquinonyl-1-hydrazine sulfonate (II) by application of the diazotization, followed by the

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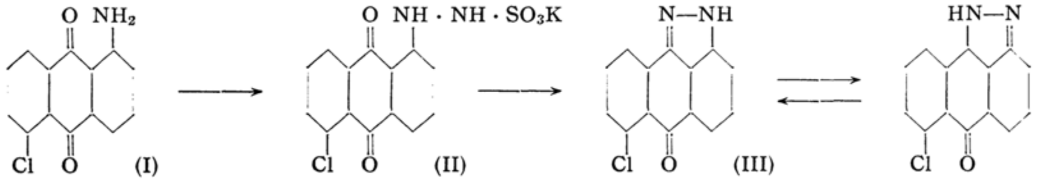
[1] Read before the 6th Annual Meeting of the Chemical Society of Japan on April 5, 1953.

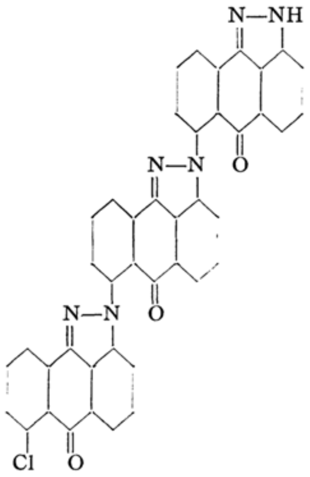
[2] Ullmann, *Ber.*, **53**, 826 (1920).

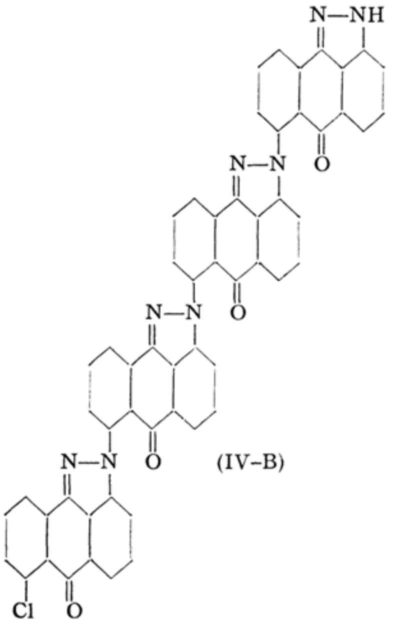
[3] *J. Chem. Soc.* **1952**, 1633.



treatment with sulfite and bisulfite and ring closure with conc. sulfuric acid analogous to our synthesis of pyrazoloanthrone from 1-aminoanthraquinone.[4] This method gives 5-chloro-pyrazoloanthrone of high purity in 79% yield of the theory. Even the crude product melted at 301–2° (corr.) and after recrystallization greenish yellow needles of m.p. 305–6° (corr.) were easily obtained.

Among the isomeric chloro derivatives of pyrazoloanthrone the 5-chloro compound is most reactive and we have found that it has an interesting behaviour of polymolecular self condensation, a new type of reaction hitherto never studied in the chemistry of anthraquinone derivatives. When 5-chloro-pyrazoloanthrone alone was heated in boiling nitrobenzene in the presence of sodium carbonate and copper for 25 hours the product was nearly 50%: 50% mixture of 3 molecular and 4 molecular self condensation product (IV-A and IV-B), which was ascertained by its properties and estimation of the terminal chlorine atoms.


(IV–A)


(IV–B)

	5-Chloro-pyrazoloanthrone(III)	Self condensation product (IV–A and IV–B)
With aq. NaOH	Orange red solution	No color reaction
m.p.	305—6°	>400°
Cl% found	13.72	4.60
In *o*-dichlorobenzene	Soluble	Insoluble
Appearance	Greenish yellow needles	Yellow brown powder
In conc. H_2SO_4	Orange	Red orange
Precipitate with water	Yellow	Yellow brown

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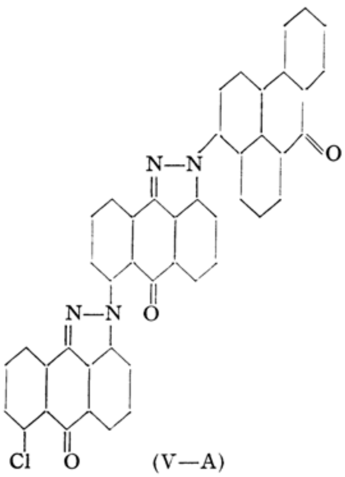
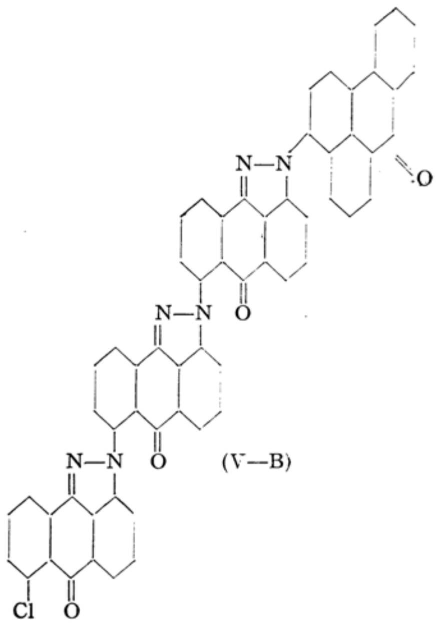
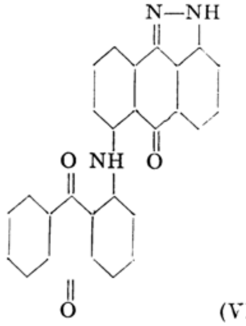
[4] T. Maki, T. Akamatsu and M. Maezawa, *J. Chem. Soc. Japan. Ind. Chem. Section*, **54**, 245 (1951).



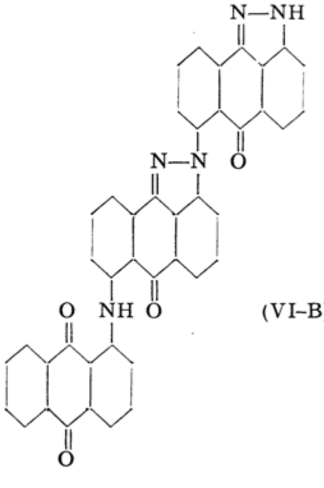
(V—A)



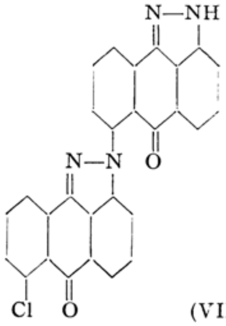
(V—B)



(VI-A)



(VI–B)



(VII)

In the presence of potassium carbonate, even without copper, the self condensation proceeded further and the obtained substance contains 3.80% Cl, which corresponds nearly to the 4 molecular condensation product (IV-B). This polymolecular self condensation occurs also in cases of other syntheses using 2 or more different components. Thus, when 5-chloro-pyrazoloanthrone and 3-bromobenzanthrone were boiled with nitrobenzene in the presence of sodium carbonate and copper for 15 hours the product was found to be a mixture of nearly 45% of (V-A) and 55% of (V-B), 1:2 and 1:3 product respectively, ascertained by the amount of recovered 3-bromobenzanthrone and estimation of Cl% and N% of the substance.

When 5-chloro-pyrazoloanthrone and 1-aminoanthraquinone were similarly boiled with naphthalene for 15 hours the chief product, insoluble in *o*-dichlorobenzene, was a mixture of nearly 34% of (VI-A) and 66% of (VI-B), 1:1 and 2:1 product respectively.

The part soluble in hot *o*-dichlorobezene, in this case, contained bimolecular self-condensation product (VII) and uncombined 1-aminoanthraquinone. The estimation of the amounts of these soluble components was useful for the determination of the proportion of (VI-A) and (VI-B).

Experimental Part

5-Chloro-pyrazoloanthrone (III).—1-Amino-

5-chloroanthraquinone (I)[5] (12.88g., 1 mol. ratio) was dissolved in 64.4g. of conc. sulfuric acid (97.0%) and sodium nitrite (3.65g., 1.06 mol. ratio), dissolved in 36.5g. of ice cold conc. sulfuric acid, was added at 2° and agitated for 30 minutes at 5°. The diazo solution was poured on 150g. of ice and after the addition of 14.6g. of anhydrous sodium sulfate stirring was continued for 30 minutes keeping the temperature below 10°. The precipitated diazo compound was filtered, agitated with 250g. of ice water and sodium bicarbonately was carefully added until the litmus-neutral point was obtained. The presence of 2 drops of lauryl alcohol is convenient as an antifoaming agent. To the neutralized diazo compound 59.0g. of 16% sodium sulfite (1.5 mol. ratio), freshly prepared from sodium hydroxide and sulfur dioxide, was added, kept 1 hour at 10°, then 1 hour at 30° and to this diazo sulfonate 21.6g. of freshly prepared 36% sodium bisulfite (1.5 mol. ratio), together with 2 cc. of conc. hydrochloric acid and 2 cc. of water, was given, warmed up to 90° and agitated at this temperature for 1 hour. The hot solution was filtered in order to remove a small amount of dark brown insoluble by-product (2.9% of the starting material) and 45g. of potassium chloride was added to the orange red filtrate and allowed to stand over night. The red crystalline precipitate of potassium 5-chloroanthraquinonyl- 1-hydrazine sulfonate (II) was collected and dried in vacuum. The yield was 21.9g. This was then dissolved in 175g. of conc. sulfuric acid (99.6%) and kept at 100° for 3 hours on a boiling water bath. 5-Chloro- pyrazoloanthrone was obtained by pouring the acid solution into water. The yield of the crude product, m.p. 301–2° (corr.), was 10.05g. or 79.0% of the theory. After recrystallization from *o*-dichlorobenzene greenish yellow needles of highest purity, m.p. 305–6° (corr.), were obtained. Its conc. sulfuric acid solution is orange, and a yellow precipitate is formed by the addition of water. Like the unsubstituted pyrazoloanthrone its imino-hydrogen is so sensitive to alkali that it dissolves in dilute sodium hydroxide with intense orange red color, which is very useful for its detection even in cases of minute quantities. As shown in our previous report[6] the tautomerism must, of course, exist also in 5-chloro-pyrazoloanthrone. Found: N, 10.74; Cl 13.72; Calcd. for $C_{14}H_7ON_2Cl$ (III): N, 11.01%; Cl 13.92%.

Self Condensation of 5-Chloro-pyrazoloanthrone.—A mixture of 1.268g. (1 mol. ratio) of 5-chloro-pyrazoloanthrone (III), 0.530g. (1 mol. ratio) of anhydrous sodium carbonate and 0.063g. (0.2 atomic ratio) of precipitated metallic copper was kept boiling with 25.4g. of nitrobenzene under reflux and stirring for 25 hours. Nitrobenzene was then removed by steam distillation and the precipitate, after collecting and drying, was dissolved in 30 times to quantity of conc. sulfuric acid and filtered through asbestos in order to remove the insoluble copper. By pouring the conc. sulfuric acid filtrate into water the condensation product was obtained, which was washed neutral and dried at 110°. The yield was 1.10g. or 86.5% of the starting material. It is a yellow brown powder of m.p. higher than 400°, with no color reaction sodium hydroxide and perfectly free from 5-chloro-pyrazoloanthrone. It is insoluble in organic solvents, soluble in conc. sulfuric acid with red orange color, and a yellow brown precipitate is formed from the acid solution by water. Found: Cl, 4.60; calcd. for $C_{42}H_{19}O_3N_6Cl$ (IV-A): Cl, 5.14%; calcd. for $C_{56}H_{25}O_4N_8Cl$ (IV-B): Cl, 3.91%. The substance corresponds neary to 50%: 50% mixture of (IV-A) and (IV-B). Contrary to 2,2'-dipyrazoloanthronyls this substance is insoluble in alkaline hydrosulfite as its constituents have no conjugation between the two carbonyls.

Condensation of 5-Chloro-pyrazoloanthrone with 3-Bromobenzanthrone.[7] — 5-Chloro-pyrazoloanthrone (2.117g., 1 mol. ratio) and anhydrous sodium carbonate (0.974g., 1.1 mol. ratio) were boiled with 31.8g. of nitrobenzene for 1 hour. The heating was interrupted for a short time, 2.834g. (1.1 mol. ratio) of 3-bromobenzanthrone together with 0.106g. (0.2 atomic ratio) of precipitated metallic copper being added, and the whole was further boiled for 15 hours. After distilling off the solvent by steam and removing the insoluble copper with conc. sulfuric acid as in the above experiment, 4.64g. of crude condensation product was obtained. As the crude product is perfectly indifferent to sodium hydroxide and gives no red color it was confirmed that it contains no more 5-chloro-pyrazoloanthrone. It was then boiled with 46.4g. of *o*-dichlorobenzene for 1 hour and filtered, when the purified condensation product, 2.32g. or 50.0% of the crude product, was obtained as the insoluble and 1.94g. (0.75 mol. ratio) of unchanged 3-bromobenzanthrone recovered from the filtrate by steam distillation. So it became known that approximately 0.35–0.4 mol. of 3-bromobenzanthrone had actually condensed with 1 mol. of 5-chloro-pyrazoloanthrone. The purified condensation product is a brown yellow powder of m.p. higher than 400°, insoluble in organic solvents and soluble in conc. sulfuric acid with orange color. Found: N,8.67; Cl, 4.28; calcd. for $C_{45}H_{21}O_3N_4Cl$ (V-A): N, 8.00%; Cl, 5.07%; calcd. for $C_{59}H_{27}O_4N_6Cl$ (V-B): N, 9.15%; Cl, 3.56%. The substance corresponds nearly to a mixture of 45% of (V-A) and 55% of (V-B).

Condensation of 5-Chloro-pyrazoloanthrone with 1-Aminoanthraquinone.[7] —A mixture of 1.015g. (1 mol. ratio) of 5-chloro-pyrazoloanthrone, 0.893g. (1 mol. ratio) of 1-aminoanthraquinone, 0.424g. (1 mol.ratio) of anhydrous sodium carbonate and 0.051g. (0.2 atomic ratio) of precipitated copper was kept boiling with 20g. of naphthalene

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[5] Obtained by the sodium sulfide reduction of 1-chloro-5-nitroanthraquinone in 91.8% yield and after recrystallization from o-dichlorobenzene melted at 219° (corr.). 1-Chloro-5-nitroanthraquinone was prepared from potassium 5-nitroanthraquinone-1-sulfonate by the chlorate method in 94% yield and a sample of m.p. 316° (corr.) was obtained after recrystallization from *o*-dichlorobenzene. See also T. Maki and Y. Nagai, *J. Chem. Soc. Ind. Japan*, **33**, 464B (1930).

[6] T. Maki and T. Akamatsu, *J. Chem. Soc. Japan, Ind. Chem. Section*, **54**, 281, 326 (1951).

[7] Compare with *G. P.* 520395, *Frdl.* **17**, 1291

under reflux and stirring for 15 hours. As in the above experiments the crude condensation product was obtained after the steam distillation of naphthalene and after removing the copper by the treatment with conc. sulfuric acid. The yield was 1.61g. The crude product is perfectly free from the starting 5-chloro-pyrazoloanthrone as it shows no red color reaction with sodium hydroxide. A small quantity of chlorine (1.5%Cl) found in the crude substance indicates the presence of about 20% of bimolecular self-condensation product (VII) (calcd. Cl 7.50%), because it can be removed by dissolving in boiling *o*-dichlorobenzene. When the crude product (1.61g.) was boiled with 48.3g. of *o*-dichlorobenzene, hot filtered 0.70g. (44% of the crude product) of chlorine free condensation product was obtained as the insoluble. From the filtrate 0.50g. of unchanged 1-aminoanthraquinone and 0.32g. of the chlorine compound (VII), corresponding to 0.34g. of 5-chloro-pyrazoloanthrone, were recovered. So it was found that about 0.39g. (0.44 mol. ratio) of 1-aminoanthraquinone had actually condensed with 0.67 g. (0.66 mol. ratio) of 5-chloro-pyrazoloanthrone. The purified, chlorine free condensation product is a red brown powder of m.p. higher than 400°, hardly soluble in organic solvents, indifferent against alkali, but soluble in conc. sulfuric acid brown, and brown red precipitate is produced from the acid solution by the addition of water. From these data it is concluded that the substance, insoluble in hot *o*-dichlorobenzene, is a mixture of nearly 34% of 1 : 1 condensation product (VI-A) and 66% of 2 : 1 condensation product (VI-B). Found: N,10.35; calcd. for $C_{28}H_{15}O_3N_3$ (VI-A): N, 9.52%; calcd. for $C_{42}H_{21}O_4N_5$ (VI-B): N, 10.62%.

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