Vat Dyes of Benzanthrone Series. XXIX.[1] *Chlorination of 16, 17-Dihydroxy-violanthrone with Phosphorus Pentachloride*

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A new attempt, a study of the reaction between 16, 17-dihydroxy-violanthrone(I) and phosphorus pentachloride, was carried out by us and certain new 16, 17-derivatives of violanthrone were obtained. They are highly interesting in the chemistry of this polynuclear system. A non aqueous colloidal suspension of 16,17-dihydroxy-violanthrone in *o*-dichlorobenzene was prepared and heated with an excess (2.5 times of the theory) of PCl_5 in a nitrogen atmosphere in order to prevent the oxidation of the two hydroxyls. The crude reaction product was a mixture of certain substances of distinctly different solubilities, which were very useful for the separation of the constituents with nitrobenzene and *o*-dichlorobenzene (see Table I).

TABLE I

SOLUBILITY RELATIONS

	Nitrobenzene		*o*-Dichlorobenzene	
Sbst.	210°	15°	180°	15°
(I)	Hardly sol.	Insol.	Practically insol.	Insol.
(II)-A,B	Insol.	Insol.	Insol.	Insol.
(III)-A,B	Sol.	Insol.	Hardly sol.	Insol.
(IV)	Sol.	Hardly sol.	Sol.	Hardly sol.
(V)	Sol.	Sol.	Sol.	Sol.

The presence of the hydroxyl in either or both of the 16,17-positions was conveniently detected by the sensitive color change of the cotton dyeings with acids and alkalis. We have found also that the absence of the hydroxyl is indicated by a water drop sensitiveness of the dyed fabrics, whereby a temporary reddish spot is produced by wetting with a water drop. Thus, for example, the initial 16,17-dihydroxy-violanthrone dyes cotton from a blue vat in clear yellowish green, which is quite indifferent against a water drop but becomes clear blue by dilute mineral acids and yellow green by dilute caustic alkalis (see Table II).

TABLE II

COLOR REACTIONS OF COTTON DYEINGS (1%)

Sbst.	Original shade	Dil. HCl	Dil.NaOH	Water drop	OH in 16.17-position
(I)	Yellowish green	Clear blue	Yellow green	Indifferent	2
(II)-A,B	Blue violet	Indifferent	Indifferent	Reddish	None
(III)-A,B	Greenish gray blue	Dark blue	Gray green	Almost indifferent	1
(IV)	Violet blue	Indifferent	Indifferent	Reddish	None
(V)	Grayish blue	Indifferent	Indifferent	Reddish	None

The part perfectly insoluble in boiling nitrobenzene is concluded as a monochloro-16,17-violanthrone-oxide (II-A of Table III), associated with a small amount of a dichloro compound (II-B). The 16,17-violanthrone-oxide is quite a new type of compound hitherto unknown in this series. The conlstitution is determined by us from the folowing facts: (1) Its blue violet color is entirely different from the yellowish green of the original 16,17-dihydroxy compound. The color change is remarkably hypsochromic. (2) It is extremely insoluble in organic solvents. Such insolubility is not found among the known blue-violet compounds of violanthrone series. (3) The hydroxyl group is absent. (4) It is sensitive to a water drop. (5) Its chlorine content is distinctly lower (found Cl, 8.68%) than that of the chlorine replacement of the 16,17-dihydroxyls to (IV) (calcd. Cl, 13.50%). (6) It is easily soluble

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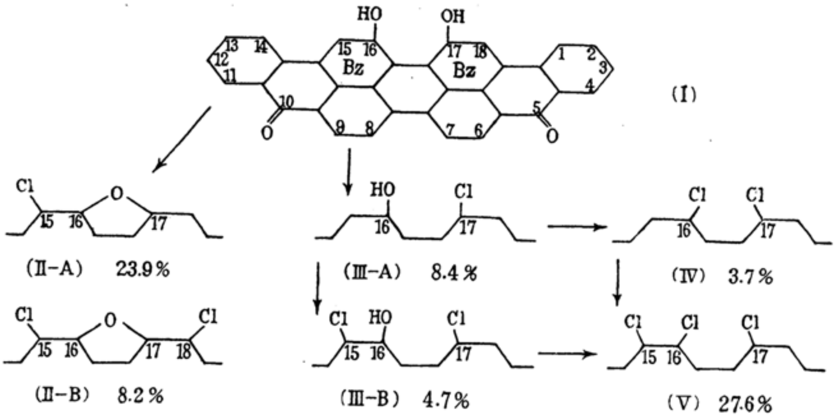
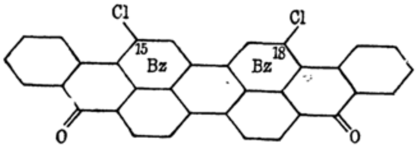
[1] Read before the 6th Annual Meeting of the Chemical Society of Japan on April 5, 1953. Cf. the preceding report XXVIII, T. Maki, *J. Chem. Soc. Ind. Japan*, **50**, 142 (1947).

TABLE III

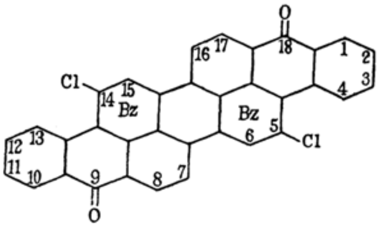
CONSTITUTION AND YIELD (% OF THE THEORY)



in alkaline hydrosulfite giving a blue vat, which proves the presence of the unchanged 5,10-dicarbonyls. (7) Considering the steric relation of 15-chloro or 15,18-dichloro group the monomolecular formula (II-A, B) is preferred by us rather than the bimolecular structure. The position of the chlorine atoms is most probably suggested as 15,18- for two reasons. One of the reasons is the ortho-orienting power of the hydroxyls and the other is our former studies on dichloro-violanthrone[2] and dichloro-isoviolanthrone[3]. Thus, when chlorination was carried out in organic solvents such as nitrobenzene, *o*-dichlorobenzene or acetic acid with free chlorine or sulfuryl chloride the chlorine atoms predominantly entered into 15,18-position of violanthrone molecule giving a clear violet vat dye (VI), and also giving the equivalent 5,14-dichloro-isoviolanthrone (VII), which is the chief constituent of Indanthrene Briliant Violet 2R and 4R.



(VI)



(VII)

Any traces of the starting material, 16,17-dihydroxy compound, were no longer found in the reaction product. The part soluble in boiling nitrobenzene but insoluble in hot *o*-dichlorobenzene is mainly 17-chloro-16-hydroxy-violanthrone (III-A), greenish gray blue dye, associated with 15,17-dichloro-16-hydroxy-violanthrone (III-B).

16,17-Dichloro-violanthrone (IV), a new, theoretically very important, violet blue substance, was obtained in minor quantity from the part soluble in hot *o*-dichlorobenzene by cooling. After chromatographic purification its yield was only 3.7% of the theory. The solubilities in organic solvents remarkably increased by the replacement of the 16,17-dihydroxyls with chlorine atoms. It is important that the color of 16,17-dichloro-violanthrone (IV) is found to be more bluish than that of violanthrone, while the 15,18-dichloro isomer (VI) is much redder than the latter. Both 16,17-and 15,18-dichloro-violanthrone give dyeings of more clear shades than those of the mother substance, violanthrone. The part easily soluble in cold nitrobenzene and cold *o*-dichlorobenzene is mainly 15,16,17-trichloro-violanthrone (V), a grayish blue vat dye.

All the above substances (I—V), which are actually substituted in Bz-rings, have blue vats and Maki's discovery [2,3] on the relation between the blue vat and Bz-substitution in violanthrone derivatives was again confirmed.

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2) T. Maki and T. Aoyama, *J. Chem. Soc. Ind. Japan, Suppl.*, 38, 636B (1935).

3) T. Maki and Y. Nagai, *Ber.*, 70, 1867 (1937).

Formerly, one of us studied the reaction between phosphorus pentachloride and 4,4'-dihydroxy-indanthrone, when the chief final product was 3,4,3',4'-tetrachloro-indanthrone[4] and 4,4'-dichloro compound was practically not obtained. It may be, therefore, a behaviour of PCl_5 that in the reactions with polynuclear anthraquinone derivatives nuclear chlorination predominates to a greater extent than the simple hydroxyl substitution. In the present case, also, trichloro-violanthrone (V) was obtained in comparatively higher yield.

The formation of the oxide ring (II-A,B), apparently by a dehydration of the two hydroxyls, is quite a special reaction between 16,17-dihydroxy-violanthrone and PCl_5. We tried to obtain a substance of the oxide type by fusing 1 part of 16,17-dihydroxy-violanthrone with 15 parts of anhydrous zinc chloride at 290°, but the result was negative. When a colloidal suspension of 1 mol. ratio of 16,17-dihydroxy-violanthrone in *o*-dichlorobenzene was boiled with 20 mol. ratio (large excess) of thionyl chloride for 12 hours the replacement of the hydroxyls with chlorine did not take place at all and only yellow green 15-chloro-16,17-dihydroxy-violanthrone (79%) was obtained together with some unchanged dihydroxy compound (21%).

Experimental Part

(1) Treatment of 16,17-Dihydroxy-violanthrone[5] with Phosphorus Pentachloride.—16,17-Dihydroxy-violanthrone (3.00 g.) was vatted with 24 g. of 25% sodium hydroxide, 5.0 g. of hydrosulfite conc. powder and 600 cc. of water by keeping at 55° for 20 minutes. The filtered vat was oxidized by a current of air and the collected precipitate, after thoroughly washed with water, was treated on the filter 3 times with methanol (20 cc., 10 cc. and 10 cc. resp.) in order to replace the water with methanol. The paste was then mixed with 150 g. of *o*-dichlorobenzene and the remaining methanol, together with about 1/3 the volume of the *o*-dichlorobenzene, was distilled off in a nitrogen atmosphere and thus a colloidal suspension of 16,17-dihydroxy-violanthrone in about 100 g. of *o*-dichlorobenzene was obtained. Phosphorus pentachloride (6.40 g., 5 mol. ratio) was added and also in a nitrogen atmosphere agitated 1 hour at room temperature, 4 hours on a boiling water bath and at last 1 hour at the boiling point of *o*-dichlorobenzene. After neutralizing with anhydrous sodium carbonate, the solvent was distilled off with steam and the collected precipitate, as a dry powder, was heated with 20 times of conc. sulfuric acid at 80° for 1 hour and then poured into water in order to hydrolyze the unstable chlorine such as $>CCl_2$ to $>C=O$. The weight of the reaction product was 3.17 g.

(2) The Part Insoluble in Boiling Nitrobenzene (II-A,B).—The crude reaction product (3.17 g.) was finely powdered and boiled with 317 g. of nitrobenzene under reflux and stirring for 1 hour and the insoluble (1.11 g.) was once more boiled with 111 g. of nitrobenzene. The yield of the final insoluble substance was 1.01 g. or 31.9% of the crude product. It is a violet black powder, entirely insoluble in boiling nitrobenzene and *o*-dichlorobenzene, soluble in conc. sulfuric acid with red violet color and dark reddish blue precipitate is formed by the addition of water. From a blue hydrosulfite vat (IN) it dyes cotton blue violet and the obtained dyeings are indifferent against acids and alkalis, but are sensitive to a water drop giving a temporary reddish spot, which disappears with the natural evaporation of water. Found: Cl, 8.68; calcd. for $C_{34}H_{13}O_3Cl$ (II-A): Cl, 7.02%; calcd. for $C_{34}H_{12}O_3Cl_2$ (II-B): Cl, 13.15%. So the substance corresponds mainly (73%) to 15-chloro-16,17-violanthrone oxide (II-A), associated with 27% of the dichloro oxide (II-B). The actual yield of (II-A) is therefore 23.9% and that of (II-B) is 8.2% of the theory.

(3) The Part Soluble in Boiling, but Insoluble in Cold Nitrobenzene.—By standing over night 0.76 g. and 0.05 g. of precipitates were obtained from the above first and second nitrobenzene filtrate respectively.

A) The Part Insoluble in Boiling *o*-Dichlorobenzene (III-A,B).—Both precipitates were combined (0.81 g. or 25.6% of the crude reaction product) and as a dry powder boiled with 81 g. of *o*-dichlorobenzene for 1 hour and the insoluble substance (0.50 g.) was once more boiled with 50 g. of the same solvent, whereby 0.41 g. (15% of the crude reaction product) of an insoluble matter was obtained. This is a violet black powder of dark blue streak and soluble in conc. sulfuric acid with red violet color. Hydrosulfite vat (IN) is blue with weak violet fluorescence and dyes cotton in greenish gray blue, which is changed by acids into dark blue and by alkalis into gray green, but is almost indifferent against a water drop. Found: Cl, 9.22, calcd. for $C_{34}H_{15}O_3Cl$ (III-A): Cl, 7.00%; calcd. for $C_{34}H_{14}O_3Cl_2$ (III-B): Cl, 13.10%. This substance is therefore composed of 64% of 17-chloro-16-hydroxy-violanthrone (III-A)

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[4] Dark violet needles from o-dichlorobenzene, in conc. sulfuric acid brown and with water blue violet precipitate. It was hardly soluble in alkaline hydrosulfite. T. Maki and T. Mine, *J. Chem. Soc. Ind. Japan*, **51**, 15 (1948).

[5] Benzanthrone (20 g.) was fused with 50 g. of KOH and 48.5 g. of isobutanol in presence of anhydr. sodium acetate (6 g.) at 110—2° for 3 hours. The crude product, as a dry powder, was boiled with 10 parts of *o*-dichlorobenzene to remove certain soluble impurities. The obtained 2, 2'-dibenzanthronyl was an olive gray powder, but of high purity, melting at 330—3° (corr.) and dissolving in conc. H_2SO_4 orange red without fluorescence. The yield was 15.8 g. (79.4% o. th.). Dibenzanthronyl (10 g.) was then dissolved in 300 g. of 84% H_2SO_4 and oxidized with 19 g. of 66% MnO_2 at 25—30° for 3 hours. The insoluble part was filtered through asbestos, thrown into water, and the obtained paste was heated with 15 g. of sodium bisulfite in 300 cc. of water and after acidification 16, 17-dihydroxy-violanthrone was collected. The yield was 8.0 g. (75.1% o. th.). The operations given in FIAT **1313**, II, 83—5 should be somewhat modified.

and 36% of 15,17-dichloro-16-hydroxy compound (III-B). The actual yield of (III-A) is 8.4% and that of (III-B) is 4.7% of the theory.

B) The Part Soluble in Boiling, but Insoluble in Cold *o*-Dichlorobenzene (IV).—When the above *o*-dichlorobenzene filtrates (3A) were allowed to stand over night 0.27 g. (8% of the crude reaction product) of a violet black precipitate was obtained. In order to make it completely free from the trace of the associated chlorohydroxyl compounds (III-A,B) it was dissolved in 54 g. of boiling *o*-dichlorobenzene, chromatographed on alumina, developed with 32.4 g. of boiling nitrobenzene, washed with 10 cc. of alcohol and the upper dark blue gray layer was eluted 5 times with each 50 g. of boiling *o*-dichlorobenzene. After steam distillation of the solvent 0.12 g. (3.6% of the crude reaction product) of a purified substance was obtained, which is a violet black crystalline powder with metallic lustre. Found: Cl, 14.53%; calcd. for $C_{34}H_{14}O_2Cl_2$ (IV): Cl, 13.50%.

The hydrosulfite vat of this substance is blue with weak violet fluorescence and dyes cotton (IN) violet blue, more bluish than violanthrone and 15,18-dichloro-violanthrone (VI). Its dyeings are quite indifferent against acids and alkalis, but are sensitive to a water drop giving a temporary reddish spot. The substance has no connection with the hydroxyl group and corresponds to 16,17-dichloro-violanthrone (IV). Contrary to the hydroxylated compounds it is soluble in hot *o*-dichlorobenzene with intense violet blue color with strong red fluorescence. Conc. sulfuric acid solution is red violet without flourescence and blue precipitate is produced from the acid solution by water. The actual yield of 16,17-dichloro-violanthrone is about 3.7% of the theory.

(4) The Part Soluble in Cold Nitrobenzene and Cold *o*-Dichlorobenzene (V).—The above cold nitrobenzene filtrates (2) were combined (ca. 428 g.) and nearly 5/6 of this solvent was distilled off. After cooling 0.27 g. of an impure precipitate was removed and the clear filtrate was distilled with steam, when 0.89 g. of a violet black powder was obtained. Found: Cl, 19.72%; calcd. for $C_{34}H_{13}O_2Cl_3$ (V): Cl, 19.01%. It dyes cotton grayish blue from a blue hydrosulfite vat (IN) and the dyed fabrics are quite indifferent against acids and alkalis, but are sensitive to a water drop. The substance is found to be 15,16,17-trichloro-violanthrone (V), free from any hydroxyl groups. It is very easily soluble in *o*-dichlorobenzene in red violet color with strong red fluorescence and is soluble in conc. sulfuric acid red violet without fluorescence. A small quantity (0.06 g.) of the same substance was also obtained from the cold *o*-dichlorobenzene filtrates of (3B) after steam distillation of the solvent. The total yield of the trichloro-violanthrone (V) is therefore 0.95 g. or 27.6% of the theory.

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