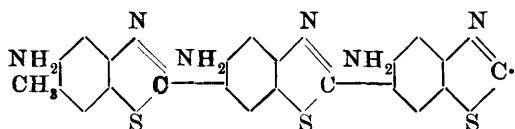


XCI.—*The Constitution of Yellow Sulphide Dyes.*

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THE following experimental work is recorded as the authors will have no further opportunity for joint work on this subject. Unfortunately, the results obtained are as yet insufficient to allow of deductions as to the constitution of these dyes.

Hitherto, no investigation on this subject appears to have been recorded. From analogy to the formation of dehydrothiitoluidine and primuline base from sulphur and *p*-toluidine, and because yellow sulphide dyes cannot be formed from *m*-phenylenediamine and sulphur, but are formed from the sulphur fusion of *m*-tolylene-diamine or acyl derivatives of *m*-phenylenediamine, it has been generally supposed that these dyes contain thiazole rings. From these ideas, one would naturally expect a considerable number of free amino-groups in the simplest sulphide dye, for example, that formed from the sulphur fusion of *m*-tolylene-diamine,



One of us found, however, that the reaction of yellow sulphide dyes with nitrous acid, either in concentrated sulphuric acid solution or freshly precipitated and in aqueous suspension, is inappreciable, and this observation led to the present investigation.

Preparation and Analysis of the Dye.

Attempts to prepare what one would suppose to be the simplest yellow sulphide dye by the fusion of *m*-tolylene-diamine and

sulphur according to D.R.-P. 139430 and 141576 gave a product with poor tinctorial properties, but a good yellow dye was obtained from the diformyl derivative of *m*-tolylenediamine by sulphur fusion according to D.R.-P. 138839, and this was used for the present investigation. The fusion product was extracted with carbon disulphide, dissolved in hot dilute sodium hydroxide solution, precipitated by hydrochloric acid, collected, washed, dried, and again extracted with carbon disulphide (Found: C* = 41.5, 41.6, 41.4; H = 3.2, 2.7, 2.5; N = 9.5, 13.4, 11.0, † 11.7 †; S = 42.3, 44.6, 42.8).

Nitrogen was evolved very slowly in the estimation by Dumas's method, and the results were consequently untrustworthy. The figures obtained by Kjeldahl's method may be taken to indicate the lowest possible value of the percentage of nitrogen.

Another sample was exhaustively extracted with carbon disulphide, but was not dissolved in alkali and reprecipitated. These steps were omitted in order to avoid the introduction of impurities, as it was found that the reprecipitated substance filtered with difficulty and could not be easily washed (Found: C = 42.9; H = 2.98; S = 42.3).

These figures indicate that the substance contains no oxygen. The proportion of carbon to nitrogen is less than in diformyl-*m*-tolylenediamine, $C_9H_{10}O_2N_2$, but greater than in *m*-tolylenediamine, $C_7H_{10}N_2$. $[(C_{17}H_{14}N_4S_{6.27})_n]$ requires C = 42.98; H = 2.95; N = 11.8; S = 42.27 per cent.]

On account of the tendency of sulphur to form polysulphide chains with any number of sulphur atoms, such a formula probably expresses the composition more correctly than one containing an integral number of sulphur atoms, but agreeing less closely with the analytical results.

Experiments on the Formation of Dye with varying Proportions of Diformyl-m-tolylenediamine and Sulphur.

The mixture was in each case heated according to D.R.-P. 138839. The products were finely powdered and washed in succession with carbon disulphide and water.

Expt. (1).—Two parts of diformyl compound and 4 parts of sulphur gave 3 parts of dye.

Expt. (2).—Two parts of diformyl compound and 2 parts of sulphur gave 1.9 parts of dye.

* C, H, and S determined together by Dennstedt's method.

† By Kjeldahl's method.

Expt. (3).—Two parts of diformyl compound and 1 part of sulphur gave 1.05 parts of dye.

In *Expt. (1)*, the proportions are those specified in the patent. The product from *Expt. (2)* was an equally strong dye, but that from (3) was much weaker.

Lead Salt.—On adding a solution of lead acetate to a solution of the dye in dilute sodium hydroxide, there was obtained a brown precipitate. This filtered very badly, but was washed first by decantation. (Found: Pb=51.0, 51.1. $C_{17}H_{10}N_4S_{6.27}Pb_2$ requires Pb=46.8 per cent.).

This result seems to indicate that there are approximately two mercaptan or acidic groups for each molecule of diformyl-*m*-tolylenediamine which has entered into the formation of the dye.

Oxidation of the Dye in Alkaline Solution with Potassium Permanganate.

One gram of the dye was dissolved in a solution of 2.5 grams of potassium hydroxide in 20 c.c. of water, and a solution of 2.5 grams of potassium permanganate in 50 c.c. of water was gradually added while the mixture was kept cool. The permanganate was immediately destroyed. The mixture was boiled and filtered hot, and the residual manganese dioxide was extracted with boiling water. On concentrating the filtrate and washings to 25 c.c. and acidifying with hydrochloric acid, sulphur dioxide was evolved, and a red precipitate was obtained, which was collected. Nothing was extracted from the filtrate by shaking with ether. The precipitate was washed with cold water and dried, first on a tile and then in an air-oven at 120° (analysis No. 1). It is somewhat soluble in cold, and almost completely so in hot, water. With the idea of preparing a purer sample for analysis, the precipitate from another preparation was boiled with excess of water and filtered hot, the filtrate was evaporated to dryness, and the residue dried in the air-oven for analysis (No. 2). This gave, however, a large quantity of ash, so it was washed with dilute hydrochloric acid and again dried and analysed (No. 3).

(1) C=42.5; H=3.57; S=29.2.

(2) C=41.7; H=4.5; S=32.1.

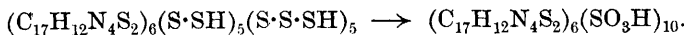
(3) C=42.1; H=3.1; S=24.9; N=11.7.

The samples contained 4.25 and 4.3 per cent. of ash respectively. The percentages are reckoned on ash-free substance.

$C_9H_8O_3N_2S_2$ requires C=42.2; H=3.1; N=10.9; S=25.0.

$C_{17}H_{14}O_5N_4S_{3.69}$ requires C=43.2; H=2.96; N=11.8; S=25.0
per cent.

The latter formula is preferred because it contains the same number of carbon, hydrogen, and nitrogen atoms as the original dye. On the most natural assumption that this substance is a sulphonic acid, we require a complex of at least $(C_{17}H_{14}N_4S_{6.27})_6$ in the dye to explain its formation, which is represented as follows:



We deduce from this that the dye complex formed from twelve molecules of diformyl-*m*-tolylenediamine contains five $\cdot S\cdot SH$ groups and five $\cdot S\cdot S\cdot SH$ groups, which are all converted into sulphonic acid groups on oxidation. There only remain twelve sulphur atoms for ring-formation, that is, one atom for each molecule of diformyl-*m*-tolylenediamine. According to this, only half the nitrogen can be involved in thiazole rings.

These conclusions are apparently opposed to those deduced from the analysis of the lead salt of the dyes, from which we inferred the presence of approximately two mercaptan or acidic groups for each molecule of diformyl-*m*-tolylenediamine concerned in the formation of the dye. It is just conceivable, however, that other atoms or groups, for example, a nitrogen atom in the ring, may exhibit acid properties.

Bases formed by the Action of Hydriodic Acid and Red Phosphorus on the Dye.

On boiling with these reagents under reflux, there is at first a little evolution of hydrogen sulphide, but, after many hours' boiling, the dye is apparently unchanged. Two and a-half grams were boiled for six hours with 0.8 gram of red phosphorus and 15 c.c. of hydriodic acid (D 1.7). The mixture was then transferred to a thick-walled glass tube, a further 0.8 gram of red phosphorus and 10 c.c. of hydriodic acid were added, the tube was sealed, and heated at 190—213° for eight and a-half hours. Much hydrogen sulphide was produced. The bulk of the hydriodic acid was distilled off, and the residue was distilled with water and filtered. On adding sodium acetate to the filtrate, a bright yellow, flocculent precipitate was formed, which was collected, washed, and dried (base *A*). On adding sodium carbonate to the filtrate and extracting repeatedly with ether, a dark brown, tarry substance was obtained (base *B*). The amount of *A* was about 0.25 gram and of *B* about 0.5 gram.

Base A.—After drying on a porous tile, this melted and decomposed at 180—200°. No crystalline acetyl derivative could be obtained from it. (Found: C=58.5; H=5.6; N=13.96; S=12.2.

834 THE CONSTITUTION OF YELLOW SULPHIDE DYES.

$C_{38}H_{44}O_5N_8S_3$ requires C=57·9; H=5·59; N=14·2; S=12·2 per cent.).

Base B.—On one occasion a few crystals were obtained by acetylating with acetic anhydride and pyridine, evaporating to dryness, and crystallising from alcohol. Attempts to obtain more crystals were, however, unsuccessful. This base contained no sulphur (and no iodine). [Found: C=61·9; H=7·37; N=8·4. M.W.=314 (determined by the cryoscopic method in glacial acetic acid solution). $NH_2=4·16$ (determined by dissolving in dilute hydrochloric acid and titrating with standard nitrite solution). $C_{17}H_{22}O_5N(NH_2)$ requires C=60·7; H=7·14; N=8·33; $NH_2=4·76$ per cent.].

By coupling the diazotised solution with β -naphthol in alkaline solution, a crimson dye was obtained, which was insoluble in dilute sodium hydroxide solution.

The presence of oxygen in these bases was unexpected. Their chemical behaviour seems inconsistent with the presence of hydroxyl or carboxyl groups. The substances were heated to constant weight at about 130° before analysis. However, if we assume the oxygen to be contained in molecularly attached water, the formulæ become $C_{38}H_{34}N_8S_3 \cdot 5H_2O$ and $C_{17}H_{12}N(NH_2) \cdot 5H_2O$. In a very approximate way, these formulæ may be interpreted as indicating that the polysulphide groups are first removed, and subsequently the cyclic sulphur is eliminated with half the nitrogen (one atom of nitrogen being removed with each atom of sulphur). As only half the remaining nitrogen is in the amino-form, the other half probably forms part of an unbroken ring connecting two benzene nuclei and not containing sulphur.

The action on the dye of tin and hydrochloric acid, zinc dust and sodium hydroxide, bromine, sodium hypobromite, phosphorus pentachloride, phosphorus pentachloride and phosphoryl chloride, phosphorus trichloride, or hot concentrated sulphuric acid has not given products which seem likely to assist in determining the constitution. Up to the present, nothing of interest has been obtained by the action of nitric acid.

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