

[CONTRIBUTION FROM THE DYESTUFF LABORATORY OF THE MENDELEEV INSTITUTE OF CHEMICAL TECHNOLOGY]

Bisulfite Compounds of Azo Dyes. V. Bisulfite Reaction of Azo Dyes Containing Two Auxochromes

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While investigating the reaction of azo dyes with sodium bisulfite, it was determined in 1911 that the presence of a naphthalene component containing an amino or hydroxy group is necessary for the formation of bisulfite compounds.¹ On treatment with bisulfite, aminoazo dyes hydrolyze, giving off ammonia, and are converted to hydroxyazo dyes which form bisulfite compounds. In refuting the hypothesis of Spiegel, accepted at that time, according to which sodium bisulfite adds on to the azo group, giving the salt of hydrazo-N-sulfonic acid of the type $RN(SO_3Na)-NHR'$, in 1915 the inadequacy of this theory was proved by a number of facts.² Of these, we consider the following most significant.

(1) The analogous physical and chemical properties of bisulfite compounds of dyes obtained by treating azo dyes with bisulfite and compounds obtained by coupling diazotized bisulfite compounds of aminonaphthols with benzene azo components (*e. g.*, phenol).

(2) The diazo dye obtained from α -naphthol and two molecules of diazotized aniline, $HOC_{10}H_5-(N=NPh)_2$, gives bisulfite compounds with only one molecule of sodium bisulfite, not with two as it should according to Spiegel, given two azo groups.

(3) All bisulfite compounds of azo dyes are colored—yellow, orange, red—while hydrazo compounds are colorless.

These and other considerations, developed in detail in former investigations, led us to the conclusion that the reactivity of azo dyes of the naphthalene series toward bisulfite is caused not by the azo group but by the auxochrome (NH_2 or OH) group in the naphthalene component of the dye and that the azo group of the dye plays a secondary role in this reaction, similar to that of the sulfo group in sulfonic acids of naphthols or naphthylamines, aiding or hindering the reaction according to the relative positions of the groups $N=N$ and the reactive group OH or NH_2 .

In a further work with S. W. Bogdanow, we

(1) N. N. Woroshtzow, *J. Russ. Phys.-Chem. Soc.*, **43**, 771 (1911); *J. prakt. Chem.*, [2] **84**, 514 (1911).

(2) N. N. Woroshtzow, *J. Russ. Phys.-Chem. Soc.*, **47**, 1669 (1915); *Ann. chim.*, [9] **6**, 381 (1916); *ibid.*, **7**, 50 (1917).

succeeded in broadening this analogy to cover the bisulfite reaction of nitrosonaphthols.³

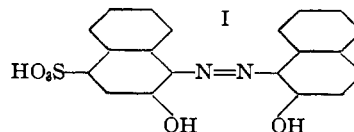
The analogous behavior of naphtholsulfonic acids and naphthol azo dyes in the bisulfite reaction was confirmed by physico-chemical investigation of the bisulfite compound of 2-naphthol-1-sulfonic acid.⁴

In the products of the reaction between bisulfite and naphtholsulfonic acids, nitrosonaphthols, or naphthol azo dyes, we find in all cases addition compounds of one molecule of bisulfite and one molecule of the original naphthol derivative. Here we definitely disagree with Bucherer who, on the basis of one incomplete analysis of the bisulfite compound of aminonaphthol, considers these compounds to be salts of acid esters of sulfurous acid and regards the reactivity of azo dyes with bisulfite from the point of view of Spiegel.⁵

Below we consider in greater detail the proof of the structure of the bisulfite compounds. Already in 1915, on the basis of the above-emphasized importance of the hydroxyl group in the reaction of the azonaphthol dye with bisulfite, it was suggested that dyes with one azo group and two hydroxyl groups can give compounds with bisulfite, containing two molecules of bisulfite and one molecule of dye.

This view has lately been disputed by A. King, an investigator who has contributed much interesting material in the field of bisulfite compounds of azo dyes.

King obtained the bisulfite compound of a dye obtained from diazotized 1,2-aminonaphthol-4-sulfonic acid and β -naphthol (I)



(3) Woroshtzow, (a) *J. Russ. Phys.-Chem. Soc.*, **61**, 497 (1929); (b) *Ber.*, **62**, 57 (1929).

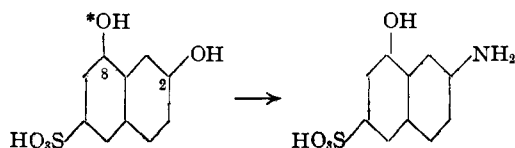
(4) N. N. Woroshtzow and A. G. Kassatkin, *ibid.*, **61**, 484 (1929); N. N. Woroshtzow and P. A. Bjelow, *J. Gen. Chem. (U. S. S. R.)*, **63**, 39 (1931); *Ber.*, **64**, 77 (1931); N. N. Woroshtzow, *Bull. soc. chim.*, [4] **35**, 996 (1924).

(5) H. T. Bucherer, *J. prakt. Chem.*, [2] **69**, 49 (1904); H. T. Bucherer and M. Schmidt, *ibid.*, [2] **79**, 385 (1909); Bucherer and E. F. Sannonborg, *ibid.*, **81**, 8 (1910); Bucherer and W. Zimmermann, *ibid.*, **108**, 285 (1921).

and found only one bisulfite group although the dye contains two hydroxyl groups.⁶

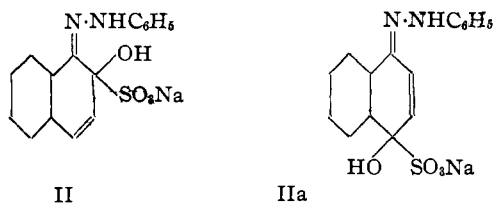
However, we do not see in King's experiment a refutation of our point of view, since the structure of this compound (I) has one peculiarity which allows us to foretell the inactivity of one of the hydroxyls, namely, the one present in the sulfonated nucleus.

It has long been known, from the work of Bucherer, that sulfo groups in the meta position to amino or hydroxyl groups in the naphthalene ring influence the bisulfite reaction unfavorably. It is possible, for example, using the ammonium salt of sulfurous acid, to exchange only one OH group for an amino group in 2,8-dihydroxynaphthol-6-sulfonic acid. Thus not diamino-



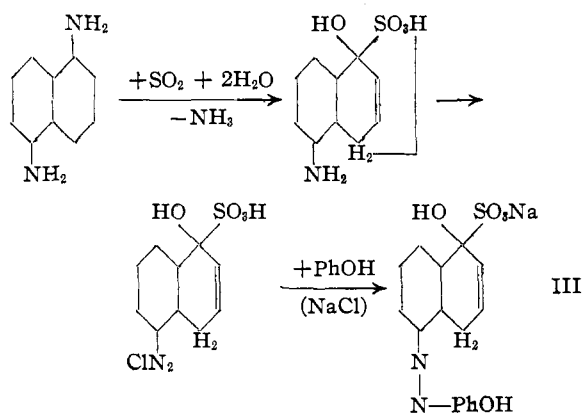
naphthalenesulfonic acid but aminonaphtholsulfonic acid is obtained, for the OH group in the 8-position marked by the star is paralyzed by the sulfo group in the meta position. Therefore we do not consider King's experiments final and have again taken up this work, formerly abandoned for various reasons, on the reactivity of monoazo dyes with two free auxochrome groups.

Before passing to a description of our experiments, we will attempt to give a short summary of the present state of the question of the structure of bisulfite compounds of azo dyes. Naphtholazo dyes give bisulfite compounds with the formula $\text{HOC}_{10}\text{H}_8\text{N}=\text{NR}\cdot\text{NaHSO}_3$. It is simplest to consider them according to the scheme corresponding to the quinoid (hydrazone) formula of azo dyes or the keto formula of naphthols, *e. g.*,

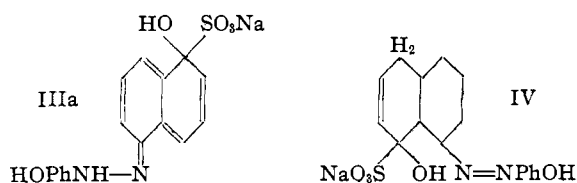


Here we employ the structure $\begin{array}{c} \text{C} \\ \text{OH} \\ \text{OSO}_2\text{Na} \end{array}$ and not the formerly used $\begin{array}{c} \text{C} \\ \text{OH} \\ \text{SO}_2\text{Na} \end{array}$, as better answering the facts on the basis of the proof of the struc-

ture of carbonyl bisulfite compounds by Raschig.⁷ But earlier we saw that bisulfite compounds of azo dyes can be formed which do not differ in physico-chemical properties from the above-mentioned compounds formed by introducing a bisulfite group into the diazo component before coupling, *e. g.*,

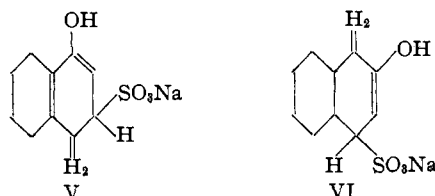


The compound III may be considered in its hydrazone form (IIIa) corresponding to anaphthoquinone



But such a transformation cannot be allowed for the analogous 1,8-aminonaphthol derivative, *e. g.*, (IV) where the quinone-hydrazone structure is excluded by the impossibility of the existence of 1,8-naphthoquinone. Later investigation of the bisulfite reaction of nitroso- β -naphthol led S. W. Bogdanow to suggest another form for the structure of naphthol bisulfite compounds and hence for bisulfite compounds of azo dyes.⁸

Bogdanow considers these compounds of α - or β -naphthol to have the structures V and VI.



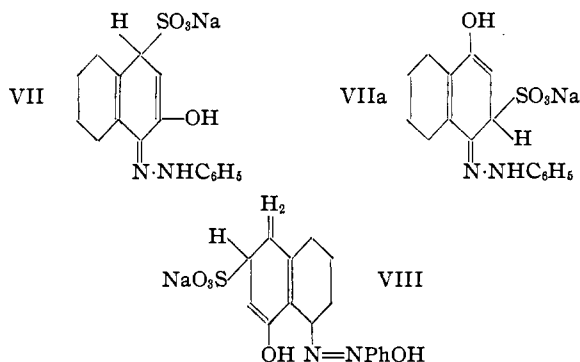
In favor of this view we note the unfavorable influence of the sulfo group in the meta-position

(7) F. Raschig, *Ber.*, **59**, 859 (1926).

(8) S. W. Bogdanow, *J. Gen. Chem. (U. S. S. R.)*, **64**, 9 (1932).

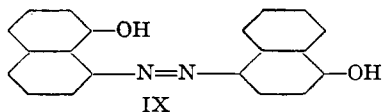
(6) A. King, *J. Chem. Soc.*, 1271 (1932).

to the OH on the formation of bisulfite compounds, which can be explained by the comparative ease with which the sulfo group enters the 4-position in reduction reactions of bisulfite β -naphthol derivatives, *e. g.*, in the conversion of the bisulfite compound of nitroso- β -naphthol to 1,2-aminonaphthol-4-sulfonic acid.⁹ According to Bogdanow the structures of the compounds II, IIa and IV are

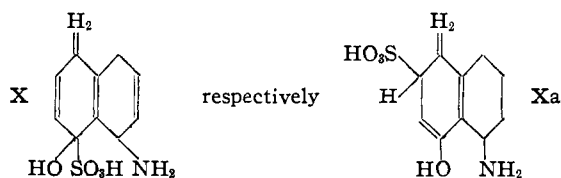


Thus, from the reactivity of the naphthalene component of azo dyes, with an OH group, we may consider permissible in various cases two different structural forms of bisulfite compounds of azo dyes—the hydrazone form in the quinoloid bisulfite (II, IIa) and hydroxyquinoidosulfonic acid (VII, VIIa) variants and the azoid form in the keto bisulfite (IV) and dihydronaphthol-sulfonic acid (VIII) variants. A final choice of variants or determination of their stability under various conditions remains to be decided by further investigation.

We set ourselves the task of studying the behavior of dyes with the structure IX in the bisulfite reaction. We shall also study mono-



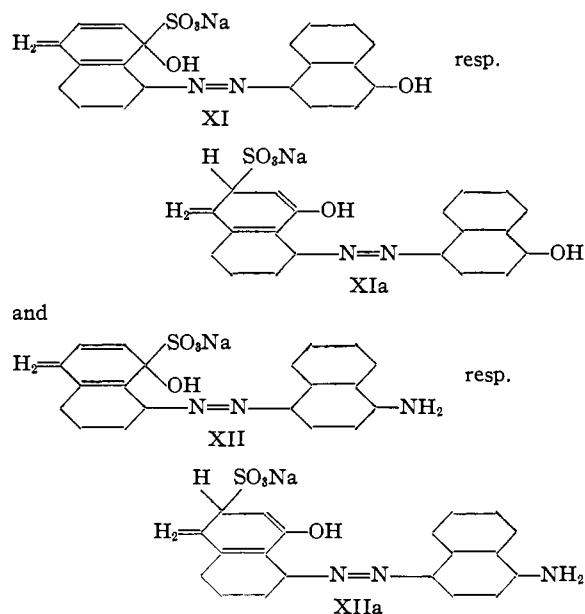
bisulfite azo dyes obtained from the diazotized compounds of X or Xa and α -naphthol or α -



naphthylamine. The bisulfite compound of 1,8-aminonaphthol (X or Xa) was obtained by one

(9) Schmidt, *J. prakt. Chem.*, [2] 44, 513 (1891); M. Boeniger, *Ber.*, 27, 23, 3050 (1894).

of the authors in 1915 from 1,8-naphthylenediamine by Bucherer's method and its composition determined by analysis. Thus dyes which are derivatives of this bisulfite compound have the structure



The diazotization of compound X takes place smoothly and quickly and requires no especially low temperatures since the diazo compound is stable. Coupling with α -naphthylamine to give the dye XII is carried out in an acid medium. An azo compound containing a bisulfite group (XII) is precipitated. On recrystallization, irregular reddish-violet needles are obtained. Coupling with α -naphthol to give the dye XI required a search for the proper medium since an alkaline soda medium affects the stability of the bisulfite radical. In an acid medium, coupling takes place very slowly. The best medium proved to be acetic acid to which a large quantity of sodium acetate was added. On recrystallization from alcohol, the orange-red dye XI precipitates in the form of fine, irregular needles. Both coupling products were treated with a 35% solution of bisulfite.

The aminoazo dye, XII, dissolves even in the cold in three to four times the theoretical amount of bisulfite solution, giving a yellow solution from which the new compound settles out in yellow crystals.

The hydroxyazo dye XI reacts only upon warming. In this case yellow crystals settle out more quickly.

The mother liquor obtained from the product prepared from the aminoazo dye contains an amount of ammonia corresponding to one molecule of ammonia for each molecule of aminoazo body.

The mother liquor from the product prepared from the hydroxyazo dyes does not contain ammonia. Therefore, the reaction of aminoazo dyes is accompanied by hydrolysis of the amino group in naphthalene dyes, in this case under extraordinarily mild conditions.

The compounds obtained from both dyes proved to be identical in composition and properties. The substance crystallizes in yellow, well-formed needles. It is soluble in water and alcohol.

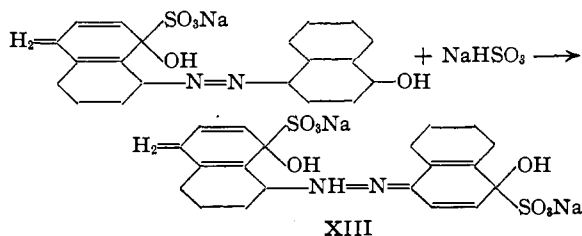
On diluting and warming the aqueous solution to 70°, the substance darkens and decomposes, giving off bisulfite. It is stable toward acids. Alkaline carbonate solutions decompose it, splitting off sulfur in the form of SO_3^{2-} ions, and a red substance is formed which crystallizes out when an excess of alkali carbonate is added. On heating the soda solution, the sulfur is completely split off as SO_3^{2-} ions, and a violet solution of a dye containing no sulfur is obtained. On treatment with caustic solutions, the substance decomposes rapidly, splitting off sulfurous acid. On heating with an excess of alkali or alkaline carbonates above 100°, a reddish-brown tarry mass is obtained.

The composition of the yellow bisulfite compound of both XI and XII is $\text{HOC}_{10}\text{H}_6\text{N}=\text{NC}_{10}\text{H}_6\text{OH}\cdot 2\text{NaHSO}_3$.

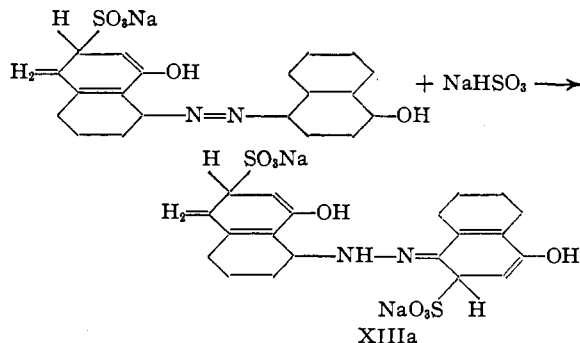
Thus the substance is an addition product of two molecules of bisulfite and one molecule of the dihydroxy dye.

In favor of this theory we cite the yellow color of the new compound compared to the red color of the original monobisulfite compound and the increased solubility in water.

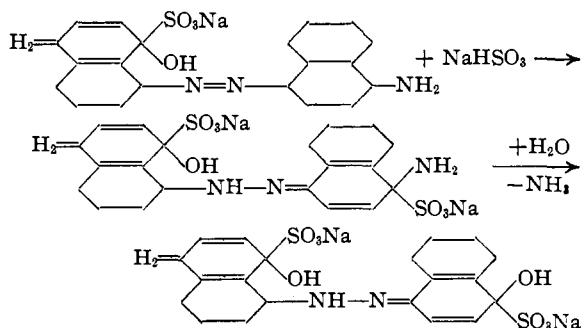
The formation of the dibisulfite compound according to the first variant may be represented as



or according to the second variant (Bogdanow)



In the reaction between bisulfite and the aminoazo dye, according to the above scheme, in which the dibisulfite compound is formed, hydrolysis of the amino group either precedes or accompanies the reaction, for example (according to the first variant)



The possibility of obtaining from compounds XIII and XIIIa first the monobisulfite compound and then the dihydroxyazo compound, free of sulfur, by stepwise hydrolysis with alkaline reagents, is in agreement with this theory of the structure of XIII and XIIIa.

On treating the water solution of the yellow dibisulfite compounds with a soda solution at a temperature not greater than 40°, the solution turns red. On adding a large excess of saturated soda solution, orange-red, irregular needle-like crystals settle out. These proved to be the monobisulfite compound of the dihydroxyazo dye. Its properties did not differ from the above-mentioned original dye (XI). Evidently the molecule of bisulfite combining with the α -naphthol nucleus is less stable than that combined with 1,8-amino-naphthol.

If the product obtained by partial hydrolysis of the dibisulfite compound is treated with bisulfite, the yellow crystalline dibisulfite compound is obtained again.

When bisulfite is split off completely from the dibisulfite compound (or the monobisulfite com-

pound XI) by treatment with an aqueous solution of soda above 70° or sodium hydroxide solution in the cold, the solution turns violet. On addition of excess concentrated sodium hydroxide solution, the monosodium compound of the dihydroxyazo dye, $\text{NaOC}_{10}\text{H}_6\text{N}_2\text{C}_{10}\text{H}_6\text{OH}$, settles out in beautiful violet needles.

It is interesting to note that it was not possible to recrystallize either the free dye or its sodium compound in sufficiently large quantities from organic solvents. As might be expected, the products obtained from the dibisulfite compounds of both the aminoazo and oxyazo dyes proved to be identical.

When the sodium compound of the dihydroxyazo dye is treated with an alcoholic water solution of bisulfite, a mixture of the same yellow dibisulfite compound described above and the monobisulfite compound is obtained. At the same time reduction processes take place which greatly lower the yield of bisulfite compound. The products of reduction were not further investigated. The presence of ammonia and an aminohydroxy compound in the reaction mixture was confirmed.

On longer treatment of the dihydroxyazo dye with bisulfite, no bisulfite compound at all could be isolated because reduction processes dominate.

Experimental

The original product, the bisulfite compound of 1,8-aminonaphthol (X) was prepared as described in our second communication by treating 1,8-naphthylenediamine with bisulfite.

(1) **Aminoazo Dye (XII) (Monobisulfite Compound).**—Two grams of compound X was dissolved in 70 cc. of water at 70°. After filtering off the insoluble residue, the hot solution was cooled. Two cc. of hydrochloric acid (sp. gr. 1.19) was then added and the mixture treated with 3.6 cc. of a 16% solution of sodium nitrite. The solution of the diazo compound is brownish-red in color.

An alcoholic solution of 1.2 g. of α -naphthylamine was prepared separately and added with rapid stirring to the solution of the diazo compound at a temperature not exceeding 12°. Stirring was continued for three hours longer. The reddish-purple dye formed on coupling settles out completely on standing at 0°. The precipitate is filtered, washed free of excess chlorine ions with water and the paste treated with bisulfite (according to 4).

The dye dissolves poorly in water and rather well in alcohol. It is difficult to crystallize it from alcohol. Only 50 mg. of reddish-violet, irregular needles was obtained from alcohol. On treatment with sodium hydroxide solution, part of the precipitate dissolves, giving a reddish-violet color. On heating it dissolves completely in the alkaline solution.

Cold soda solution has no effect in the cold. On heating, a reddish-violet solution is formed.

The dye undergoes no change on treatment with hydrochloric acid.

(2) **Hydroxyazo Dye (XI) (Monobisulfite Compound).**—To the solution of diazo compound prepared in (1) from 2 g. of compound X a solution of sodium acetate was added to neutralize the hydrochloric acid. The solution was tested with congo red. Five cc. of acetic acid (80%) and 8 g. of crystalline sodium acetate were then added. A solution of 1.4 g. of α -naphthol in 12 cc. of water containing 0.4 g. of sodium hydroxide was added gradually, and an orange-red solution was formed. A crystalline dye settles out of the solution almost quantitatively on allowing to stand in the cold (-5°) for twenty-four hours and adding 10 g. of solid sodium chloride. The precipitate was filtered, washed with small portions of ice water and the paste treated with bisulfite. If coupling with α -naphthol is carried out in acetic acid solution without adding sodium acetate (or adding only a small amount of sodium acetate), the reaction is slowed up considerably and will go to an end on addition of an excess of α -naphthol. About four times the theoretical quantity of α -naphthol is required. However, the yield is small, and the product is contaminated by α -naphthol. On coupling with α -naphthol in sodium bicarbonate solution, the same results are obtained.

The dye dissolves fairly well in water, giving an orange-red solution. It dissolves readily in hot and cold alcohol. It does not crystallize well from alcohol. Only 30 mg. of pure substance was obtained in the form of fine, needle-like, reddish-orange crystals.

The dye does not dissolve in cold soda solution but gives a violet solution on heating. A deep violet solution is obtained on dissolving the dye in cold or hot sodium hydroxide solution.

On heating above 75°, the neutral aqueous solution darkens and becomes orange-brown in color. The dye is unchanged by hydrochloric acid.

Determination of sulfur in the bisulfite group of the dye is carried out in all cases in the following manner. A sample, weighed exactly, is dissolved in a definite volume of water so as to obtain a very dilute solution (0.005–0.01%) since at higher concentrations the violet color of the solutions makes it difficult to titrate with starch. A definite volume is treated with excess sodium hydroxide solution and heated for half an hour to 75°.

The sodium sulfite formed is titrated iodometrically. The solution containing the sulfite is added from a buret to a 0.01 N solution of iodine acidified with hydrochloric acid to disappearance of the blue color.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{SO}_4\text{Na}$: S, 7.65. Found: S, 7.24.

(3) **Dihydroxyazo Dye (IX) (1,5'-Dihydroxy-4,4'-azo-naphthalene).**—Ten cc. of a solution of the diazo compound obtained according to (1) from 2 g. of compound X, was treated with an excess of alkali (5 cc. of a 30% sodium hydroxide solution). The solution turned deep red. The theoretical quantity of α -naphthol (1.2 g. of α -naphthol + 0.34 g. of NaOH + 10 cc. of water) was added gradually to the solution. Coupling takes place rapidly. However, the dye does not settle out quantitatively even after standing for twenty-four hours in the cold. When the mixture is treated with excess hydro-

chloric acid, the dye settles out quantitatively in the form of a reddish-violet powder, which gives with concd. sulfuric acid a bluish-green solution.

(4) **Dibisulfite Compound of the Dihydroxyazo Dye (XIII).** (a) **Preparation from the Aminoazo Dye (XII).**—A paste of the dye (prepared as in (1)) was shaken with 10 cc. of 35% sodium bisulfite solution at room temperature. The dye gradually goes into solution, and the color, which is orange-brown at first, turns orange-yellow. After eight to ten hours the dye is dissolved completely. On further standing, light yellow crystals of the dibisulfite compound settle out. When tests taken from the reaction mixture were observed under the microscope, the gradual disappearance of the reddish-violet crystals of monobisulfite compound and the precipitation of the yellow needles of dibisulfite compound could be followed. After three to four days the precipitation of the product is complete and the solution turns yellow. The crystals were filtered off, washed with small quantities of ice water and dried at room temperature over sulfuric acid in a desiccator. On drying with exposure to air above 40–50°, the product turns brown. When alkali is added to the mother liquor, ammonia is liberated.

The dibisulfite compound cannot be precipitated from the mother liquor by addition of sodium chloride. After half the water had been distilled off *in vacuo*, a mixture of crystals of sodium bisulfite and dibisulfite compounds settled out. When all the water had been distilled off at 35°, the residue was extracted with absolute alcohol to which 2 cc. of glacial acetic acid had been added. After filtering off the mineral salts, three-fourths of the alcohol was distilled off. On standing in the cold, orange-yellow crystals settled out of the remaining solution. These crystals were darker than those obtained in the first crop.

Quantitative Determination of the Ammonia Obtained by Hydrolysis of the Aminoazo Dye (XII) with Bisulfite.—A small quantity of thoroughly washed dye paste was dried to constant weight at 40° and a sample of the dry substance (0.5240 g.) mixed with 5 cc. of 35% sodium bisulfite solution and allowed to stand overnight. After twenty-four hours the mixture was treated with a large excess of sodium hydroxide solution and heated to boiling, the ammonia liberated being absorbed in 75 cc. of 0.04 *N* hydrochloric acid solution. The excess hydrochloric acid was titrated with 0.1 *N* sodium hydroxide solution. Calcd. for $C_{20}H_{14}N_2(SO_2Na)NH_2$: NH_3 , 4.2. Found: 3.9.

Iodometric Determination of Sulfur (see above).—Calcd. for $C_{20}H_{16}N_2S_2O_3Na_2$: S, 12.26. Found: S, 11.15.

(b) **Preparation from Hydroxyazo Dye (XI).**—To a paste of the dye (obtained from 2 g. of the bisulfite compound of 1,8-aminonaphthol according to (2)) was added 10 cc. of 35% sodium bisulfite solution and the mixture refluxed on a water-bath at 70°. After three hours the precipitate gradually dissolved.

After heating for twenty-four hours, the red crystals of the monobisulfite compound in the mixture disappeared, and their place was taken by pale-yellow crystals of the dibisulfite compound. The course of the reaction was followed under the microscope by observing test samples taken every hour.

The yellow crystals were filtered off, washed with a small

quantity of ice-water, and dried at room temperature in a desiccator. On standing, a small quantity of yellow crystals settled out of the mother liquor. No ammonia was liberated on warming the mother liquor with alkali.

The dibisulfite compounds obtained according to (a) and (b) are absolutely identical. The compound is readily soluble in water, giving a yellow solution. It is readily soluble in alcohol. Its solubility in hot and cold alcohol is almost the same. It is difficult to recrystallize the compound from alcohol but it crystallizes from water in long pale yellow needles. The product was purified by recrystallization from small portions of alcohol. On cooling, only 60 mg. of pure substance was obtained.

Long boiling with alcohol or concentration of the alcohol solution of the product by distillation even *in vacuo* causes the product to darken and lose its crystalline form.

On heating with soda or sodium hydroxide solution, a violet solution is obtained. A solution of the dibisulfite compound does not change color on treatment with hydrochloric acid in the cold; on heating it reddens noticeably.

On heating 0.5–2% water solutions of the dibisulfite compound to 65°, the solutions redden.

Iodometric Determination of Sulfur.—Calcd. for $C_{20}H_{16}N_2S_2O_3Na_2$: S, 12.26. Found: S, 11.40.

(c) **Preparation from 1,5'-Dihydroxy-4,4'-azonaphthalene (IX).**—A paste of the dye obtained according to (3) undergoes no change when treated with bisulfite solution in the cold. On long heating at 70–95° the solution turns orange-brown, and the product is converted to a tarry mass. The reaction with sodium hydroxide indicates the presence of only traces of bisulfite compound. Ammonia was found in the reaction mixture. A solution of ferric chloride gives a dirty blue color with the reaction mixture.

Better results were obtained when four times the required amount of sodium bisulfite in alcoholic water solution (ratio of alcohol to water 3:2) was used and the mixture heated to 70° at a pressure of 100–120 mm.

After ten hours most of the dye had dissolved, giving a brown solution. Part remained in the form of black, tarry lumps. After filtering the cooled solution and allowing it to stand for twenty-four hours, a large quantity of orange-yellow crystalline bisulfite compound settled out. The course of the reaction was controlled by observing test samples of the reaction mixture under the microscope. The product was collected and dried as described above. It consisted of a mixture of mono and dibisulfite compounds.

(5) **Hydrolysis of the Dibisulfite Compound of 1,5'-Dihydroxy-4,4'-azonaphthalene.** (a) **Partial Hydrolysis.**—Two grams of dibisulfite compound prepared according to 4a and 4b was dissolved in 25 cc. of water, treated with 30 cc. of saturated soda solution in the cold and heated to 40°. The solution turns orange-red. After ten to fifteen minutes no further precipitation takes place. Sodium chloride and soda precipitate no more crystals from the filtrate. The crystalline precipitate is washed with ice water and dried as above.

The compound does not differ from the one described in (2) in crystalline form, solubility in water and alcohol, behavior toward alkalis and acids, behavior of its solutions on heating.

Iodometric Determination of Sulfur.—Calcd. for $C_{20}H_{13}N_2SO_3Na$: S, 7.65. Found: S, 7.31.

Two grams of the monobisulfite compound was treated with 10 cc. of 35% sodium bisulfite compound at 70°. After twenty-four hours the product dissolved completely. Yellow needles in all respects similar to those obtained in (4) settled out of the solution.

When treated with bisulfite in the cold, the monobisulfite compound is not converted to the dibisulfite compound even after forty-eight hours.

(b) **Complete Hydrolysis.**—The same results are obtained from hydrolysis of both the monobisulfite and dibisulfite compounds of 1,5'-dihydroxy-4,4'-azonaphthalene (XI).

One gram of the bisulfite compound was treated with 10 cc. of 25% sodium hydroxide solution. Very fine violet needles settled out in the cold, and on heating with excess sodium hydroxide, a violet solution was obtained. On cooling this solution, large violet needles with a metallic luster settled out. The product was recrystallized from hot alkali solution, washed with water to neutral reaction, and dried at 100°. According to the analysis, the product is the monosodium salt of the dihydroxyazo dye.

Analysis of the products obtained from the dibisulfite (1) and monobisulfite (2) compounds of the dihydroxyazonaphthalene: (1) Calcd. for $C_{20}H_{13}N_2O_2Na$: Na, 6.84; N, 8.5. Found: Na, 6.95; N, 8.3. (2) Calcd. for $C_{20}H_{13}N_2O_2Na$: Na, 6.84. Found: Na, 7.04.

On treating the hot (80°) alkaline solution of the dye with excess hydrochloric acid, all of the dye settles out in the form of reddish-violet powder which is absolutely identical with the product obtained in (3). The precipitate is washed thoroughly with water and dried at 100°.

The monosodium compound of the dye is insoluble in both hot and cold water, readily soluble in alcohol, ether, ethyl acetate and chloroform. It dissolves with difficulty in cold, better in hot benzene, toluene, nitrobenzene and glacial acetic acid. It is insoluble in cold alkalies but dissolves completely in hot alkalies. It is insoluble in both hot and cold soda solution.

The free dihydroxyazo dye behaves like the sodium compound toward solvents.

Summary

1. It has been shown, contrary to the statement of A. King, that it is possible to obtain addition products containing two molecules of bisulfite from monoazo dyes with two auxochromes. This proves the dominant importance of the auxochrome group (and the nucleus containing it) in the reaction of naphthaleneazo dyes with bisulfite and disproves Spiegel's theory.

2. The dibisulfite compound of the dye prepared from diazotized 1,8-aminonaphthol and α -naphthol may be obtained easily from the monobisulfite compound. Due to side reactions, a pure product cannot be obtained from the dye which contains no bisulfite group.

3. The formation of the dibisulfite compound from the monobisulfite compound of the α -naphthylamine dye is accompanied by hydrolysis of the amino group and the transition of the organic nucleus to the dihydroxy dye.

4. On hydrolysis of the dibisulfite compound of the dye in alkaline solution, stepwise decomposition takes place. First one molecule of bisulfite splits off, giving the monobisulfite compound. Then the second molecule splits off, forming the free dye.

5. The formation of bisulfite compounds corresponding to both the azoid and hydrazone forms is possible.

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Preparation and Properties of Xyloseen-(1,2) Tribenzoate

BY RANDOLPH T. MAJOR AND ELMER W. COOK

In the course of the investigation of various new syntheses of ascorbic acid an attempt was made to prepare xyloseen-(1,2) triacetate. Only a gum was obtained. The preparation of xyloseen-(1,2) tribenzoate was then undertaken in the hope that it might crystallize. This proved to be the case. Xyloseen-(1,2) tribenzoate was prepared by a procedure similar to that described by Maurer and Petsch¹ for the preparation of glucoseen tetrabenzoate.

(1) Maurer and Petsch, *Ber.*, **66**, 998 (1933).

Experimental

***d*-Xylose Tetrabenzoate.**—*d*-Xylose (50 g.) was added gradually to a mixture consisting of 190 cc. of benzoyl chloride, 200 cc. of anhydrous pyridine and 380 cc. of anhydrous chloroform, cooled in an ice-bath. The xylose soon dissolved and the solution was allowed to stand for twenty-four hours. Chloroform (600 cc.) was then added and the solution was washed successively with cold dilute sulfuric acid, sodium bicarbonate and water. After drying over calcium chloride the chloroform was removed by evaporation *in vacuo*. The crystalline residue of α -*d*-xylose tetrabenzoate was recrystallized from dioxane with the addition of methanol. It was also recrystallized either