

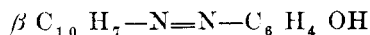
ON THE ACTION OF DIAZO- $\beta$ -NAPHTHALENE ON PHENOLS.

By J. H. STEBBINS, Jr.

Since the discovery, that  $\beta$ -naphthole could be converted into  $\beta$ -naphthylamine by the action of ammonia, under pressure, a new field for the production of azo-colors has been opened up. These compounds would, of course, be isomeric with those derived from  $\alpha$ -naphthylamine, or rather diazo- $\alpha$ -naphthalene.

It has been mentioned by several writers that  $\beta$ -naphthylamine may be diazotized, and combined with phenoles, to form new azo-compounds, but in no case have any such compounds been described.

Being desirous of obtaining an insight into the nature of these bodies, I treated diazo- $\beta$ -naphthalenechloride with such phenoles as I had at command, and obtained the following results :

*Phenol-azo- $\beta$ -naphthalene.*

This compound was obtained as follows :

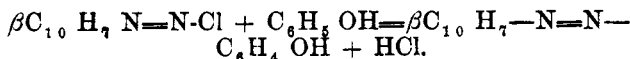
10.2 grms.  $\beta$ -naphthylamine were dissolved in 12.7 grms. HCl. (1.2 Sp. Gr.), diluted with 500 c. c. water at gentle heat filtered, and allowed to cool.

When cold, the solution was treated, under constant stirring, with 5 grms. Na NO<sub>2</sub> dissolved in 50 c. c. water.

The diazo- $\beta$ -naphthalenechloride thus formed was allowed to rest for an hour, and then mixed with a solution composed of phenol 6.7 grms., Na OH 5.7 grms., and water 200 c. c. A brick-red precipitate was immediately formed. This was collected on a filter and allowed to dry. It was purified by dissolving it in NaOH and water, reprecipitating it with acetic acid, and finally crystallizing from benzene.

It is deposited from this solvent in groups of small, pale-yellow, cigar-shaped crystals, slightly soluble in cold water, and melting to a resinous mass in boiling water. It dissolves freely in caustic soda, from which it is reprecipitated unaltered by acids, is soluble in alcohol with a yellow color, and in strong sulphuric acid with a deep crimson color. Melting point about 100° C.

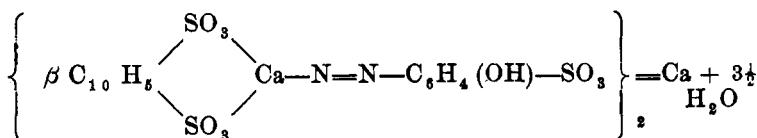
The body is probably formed according to the following equation :



On heating one part of the dyestuff with 3 pts. of fuming sulphuric acid, on the water bath for about an hour, a sulpho-acid is formed. The melt is dissolved in water, neutralized with  $CaCO_3$ , and filtered from the  $Ca SO_4$ .

The filtrate, on being concentrated by evaporation, deposits when cold the acid lime salt of the new sulpho-acid as a network of microscopic needles, which by transmitted light appear yellow, and in reflected light red-brown.

Determinations of S and Ca prove this body to be the acid Ca salt of phenol-azo- $\beta$ -naphthalenetrisulpho-acid.



Found.

(1.) 0.8703 grm. substance lost on drying at  $110^\circ C$ . 0.0577 grm. of water, =6.6% =  $3\frac{1}{2}$  mols.  $H_2 O$ .

(2.) 0.8126 grm. anhydrous salt gave 0.333 grm.  $Ca SO_4$ . Equivalent to calcium 0.097 grm. or Ca—11.93%.

(3.) 0.5 grm. anhydrous salt gave  $Ba SO_4$  0.4648 grm. Equivalent to sulphur 12.76%.

Theory requires.

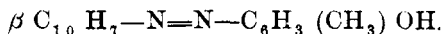
Calcium .....	12.87%
Sulphur .....	13.73%

Although the figures obtained are somewhat too low, yet I have no hesitation in pronouncing the new compound to be constituted as above set forth, as the figures obtained are too high for a disulpho-acid, and much too low for a tetrasulpho-acid, which requires 19.8% sulphur. The discrepancy in the figures is probably due to some impurity in the compound examined, which I had not perfectly removed. The free sulpho-acid (assuming the above to be correct) would, therefore, be represented by one of the following formulae :

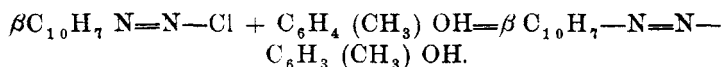
1.  $\beta C_{10} H_7 (HSO_3)_2 -N=N-C_6 H_3 (HSO_3) OH$ .
2.  $\beta C_{10} H_7 (HSO_3) -N=N-C_6 H_2 (HSO_3)_2 OH$ .

Which of the above two formulae is the correct one, I have thus far not been able to decide. The formation of a diazo-compound was not observed.

*Orthocresol-azo- $\beta$ -naphthalene.*

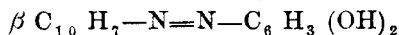


10.2 grms.  $\beta$ -naphthylamine were diazotized with 12.7 grms. H Cl (1.2 Sp. Gr.) and 5 grms. sodium nitrate, and the solution thus obtained, after resting for an hour, was added to a solution composed of ortho-cresole 7.7 grms., caustic soda 5.7 grms. and water 200 c. c. A copious, brownish-yellow, precipitate was immediately formed. It was collected on a filter, washed and dried. It dissolves in toluene, ether, petroleum ether, alcohol, and glacial acetic acid, but does not crystallize from any of these solvents. It is soluble in caustic soda, and is reprecipitated unaltered by dilute acids. It melts in boiling water to a resinous mass, undergoing at the same time partial decomposition. Heated on the water bath with fuming sulphuric acid, it undergoes total decomposition, so that a sulpho-acid could not in this case be produced. For lack of material I was unable to analyse it, but have no doubt that it is formed according to the following reaction :



Owing to the unsatisfactory nature of this body, it was not further investigated.

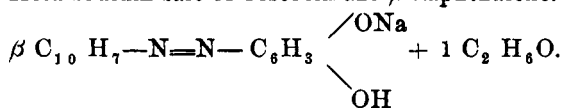
*Resorcin-azo- $\beta$ -naphthalene.*



10.2 grms.  $\beta$ -naphthylamine were dissolved in 12.8 grms. H Cl (1.2 Sp. Gr.) diluted with 500 c. c. water, and diazotized with 5 grms.  $\text{Na NO}_2$ . The  $\beta$ -diazonaphthalenechloride thus obtained was added, under constant stirring, to a solution composed of resorcline 7.8 grms., caustic soda 5.7 grms. and water 200 c. c. A red-brown precipitate was immediately formed. This was collected on a filter, washed, dried, and finally treated with caustic soda, which dissolves a part of the precipitate. The insoluble residue was washed, dried, and set apart for further examination. The filtrate was acidified with HCl, which threw down a yellow-brown precipitate ; this precipitate is the acid, soda salt of resorcin-azo

$\beta$ -naphthalene. It was collected on a filter, washed with cold water, dried, and dissolved in alcohol, from which on cooling it crystallises in bunches of microscopic, yellow needles, which melt at  $200^{\circ}$  C., undergoing total decomposition. This compound probably has the following formula, and agrees very closely with the figures obtained by analysis :

Acid sodium salt of resorcin-azo- $\beta$ -naphthalene.



Found.

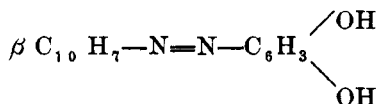
Nitrogen..... 9.53%

Theory.

Nitrogen..... 9.79%

It crystallizes with one molecule alcohol of crystallization, as will be seen from the analysis.

0.463 grm. substance lost on drying at  $110^{\circ}$  C. .002 grm. alcohol, = 0.45%, = 1 mol.  $\text{C}_2\text{H}_6\text{O}$ . The free acid would, therefore, have the formula



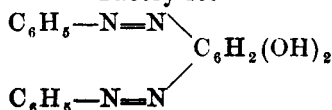
On being heated with 3 pts. of fuming sulphuric acid on the water bath for 3 hours, a sulpho-acid is formed, which, for want of time, I have not further investigated.

The residue insoluble in caustic soda, referred to above, was dissolved in alcohol, which, on being concentrated, deposited the new compound, in the shape of flat, reddish-brown prisms. Melting point  $143-144^{\circ}$ . It was first thought that this substance might be a diazo-compound, but a nitrogen estimation proved this not to be the case.

Found

Nitrogen..... 4.4%

Theory for



Nitrogen..... 13.4

The exact nature of this compound I have as yet not discovered, but hope to do so in future.

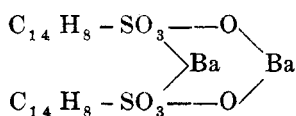
### ON BETAPHENANTHROLMONOSULPHO-ACID.

By WM. RUPP.

This acid was prepared by heating one part of  $\beta$  phenanthrol (Morton and Geyer, Jour. Am. Chem. Soc., II., 205) with two parts of sulphuric acid, on the water bath for five hours. The resulting product was dissolved in water, neutralized with lead carbonate, and the sulpho-acid set free, by precipitating the lead with sulphuretted hydrogen. The free acid,  $C_{14}H_8(HSO_3)OH$  is soluble in water, alcohol and ether, but could not be obtained in a crystalline form. After the solvent had evaporated it always formed a black, pitch-like mass, even when the concentrated solution was quite light in color. All attempts to decolorize it were unsuccessful.

The lead salt is slightly soluble in cold water, and quite soluble in boiling water.

With an excess of barium hydrate, a light grey amorphous precipitate is formed, which was found to be the neutral barium salt.



Theory,	Ba	44.1
Found,	Ba	42.5

The barium salt is insoluble in cold and boiling water and in acids.