FOUND.

Carbon	52.19 per cent.
Hydrogen	6.10 "

BY-PRODUCT.

The by-product heretofore described was dissolved in boiling water, and neutralized with $PbCO_3$.

The precipitate of $PbSO_4$ was collected on a filter, and the clear filtrate treated with a current of H_2S, till all the lead had been thrown down as PbS. This was collected on a filter, and the filtrate evaporated to the consistency of a syrup. It was then placed over sulphuric acid and allowed to crystallize. The compound so obtained crystallizes in long, white needles, which bear a striking resemblance to the disulpho acid of alpha thymole. They are very easily soluble in water, and are likewise quite hygroscopic.

Owing to the small amount of substance under examination, a combustion was out of question, but to judge from the appearance of this body, I should immediately call it alpha thymole disulpho-acid

XXIX.—ON THE COMBINATION OF DIAZO COMPOUNDS WITH ALPHA THYMOLE SULPHO-ACID.

By JAMES H. STEBBINS, JR.

In my last paper I hinted at the possibility of combining diazo compounds with alpha thymole sulpho-acid, and I will take the liberty, on this occasion, of describing my experiments in this direction.

Azobenzole alpha thymole sulpho-acid,

$$C_6H_4 - N = N - C_6H(CH_3)(C_3H_7)(HSO_3)OH.$$

9.3 grms. aniline were dissolved in 22 grms. of strong HCl, diluted with 200 c.c. of water. To this mixture was then added, under constant stirring, 7 grms. of $NaNO_2$, previously dissolved in 50 c.c. of water.

The diazobenzole chloride thus formed was added gradually to an alkaline solution of the soda salt of alpha thymole sulpho-acid, consisting of 23.6 grms. of the sulpho acid and 8 grms. of KOH, previously dissolved in 200 c.c. of water. A copious yellow precipitate, composed of minute hair-fine needles, is thus formed, and constitutes the soda salt of our new dye-stuff.

This was then dissolved in boiling water and filtered from a black tarry fluid which was formed during the dissolving process. This tarry fluid solidifies on cooling into a black mass, and evidently indicates that a decomposition of some kind had taken place.

The clear filtrate, when cold, deposits the soda salt of our new substance in the form of a network of minute, hair-fine, yellow needles. They were then collected on a filter, washed and dried at 100° C. When dry they take on a fine, metallic golden lustre, but their yellow color is changed to red-brown by the action of heat, which, however, does not destroy their tinctorial properties. This salt is easily soluble in water, and alcohol, and dyes wool of a pretty yellow color, in an acid bath. The formation of this substance may be explained, theoretically speaking, as follows:

$$C_6H_5N_2Cl + C_6H_2(CH_3)(C_3H_7)(NaSO_3)ONa =$$
$$C_6H_5 - N = N - C_6H(CH^3)(C_3H_7)(NaSO_3)OH) + (NaCl.$$

A combustion of the above gave:

THEORY.

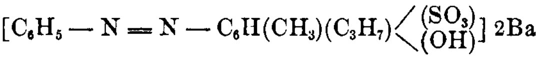
C_{16}	192	53.93	per cent.
H_{17}	17	4.77	"
N_2	28	7.86	"
S	32	8.99	"
Na	23	6.46	"
O_4	64	17.99	"
	356	100.00	

FOUND.

Carbon	53.77	per cent.
Hydrogen	4.72	"
Nitrogen	8.71	"

A sulphur estimation gave: 0.2060 grm. substance gave 0.1350 grm. $BaSO_4$, which is equal to sulphur 8.99 per cent.

BARIUM SALT.



$$[C_6H_5 - N = N - C_6H(CH_3)(C_3H_7)\left\langle\begin{matrix}(SO_3)\\(OH)\end{matrix}\right] 2Ba$$

A part of the soda salt was dissolved in boiling water, and treated with an excess of $BaCl_2$. This threw down the barium salt as an amorphous yellow precipitate. This was collected on a filter, washed several times, and then treated with boiling water.

As soon as the fluid cools, the barium salt crystallizes in hair-fine yellow needles. These are insoluble in cold, and only sparingly soluble in boiling water, but quite soluble in 90 per cent. alcohol.

A barium estimate was made, in order to ascertain the true molecular weight of the free acid, as well as to verify the assumed formula of the barium salt. 0.0902 grm. of substance gave 0.0238 grm. ash, or :

Barium	18.35 per cent.

THEORY.

Barium........	18.40 per cent.

This proves, beyond doubt, the correctness of the formula above set forth.

FREE ACID.

$$C_6H_5-N=N-C_6H(CH_3)(C_3H_7)(HSO_3)OH.$$

A portion of the soda salt was dissolved in boiling water, and treated with an excess of strong HCl.

This threw down the free acid as a red amorphous precipitate, which, when dry, has a beautiful, golden-red, metallic lustre. The precipitate was then collected on a filter, and dissolved in boiling water. The hot solution so obtained was filtered, to separate it from a black resinous substance which seemed to be formed by the decomposition of the free acid while boiling with water. The filtrate, when cold, deposited the free dye-stuff, in the form of minute yellow, six-sided prisms. This body melts at 215¾° C., with total decomposition. When heated on platinum foil, it burns with a red flame, and evolves copious yellow fumes, while on the foil is left a very difficultly combustible carbon residue. This interesting new dye-stuff, although of no commercial value, fully sustains the theory that we advanced in the beginning of this paper, namely, that diazo compounds can be made to combine with phenoles of the kind referred to.

The constitution of this compound can be explained from its reduction products. When treated with reducing agents, as zinc dust, or tin and HCl, the solution is decolorized, probably forming aniline, and amido-thymole sulpho-acid. This latter, however, I have failed to isolate, as the quantity of material unde examination was too small.

Parazotoluole alpha thymole sulpho-acid.

$$C_6H_4(\overset{4}{C}H_3)\overset{:}{-}\overset{1}{N}=N-C_6H(CH_3)(C_3H_7)(HSO_3)OH.$$

10.8 grms. of paratoluidine were dissolved in 22 grms. of strong HCl, diluted with 200 c.c. of water.

To this was then added, under constant stirring, 7 grms. of $NaNO_2$, previously dissolved in 50 c.c. of water.

The paradiazotoluole chloride thus formed, was allowed to rest for a while, and then mixed with 23.6 grms. of the soda salt of alpha thymole sulpho-acid, previously dissolved in 200 c.c. of water, made alkaline with 8 grms. of NaOH.

A copious yellow precipitate of the soda salt of parazotoluole alpha thymole sulpho-acid is formed. This was then collected on a filter, washed and dissolved in boiling water.

This compound is partially decomposed by boiling water, in the same manner as the previously described body.

The filtrate of the above when cold, deposits the soda salt in hair-fine, yellow-brown needles.

It is nearly insoluble in cold, but more soluble in boiling water.

It melts far above the boiling point of strong H_2SO_4.

The formation of this substance may be explained from the following reaction.

$$C_6H_4(CH_3)NCl + C_6H_2(CH_3)(C_3H_7)(NaSO_3)ONa =$$

$$C_6H_4(\overset{4}{C}H_3) \overset{:}{—} \overset{1}{N} = N — C_6H(CN_3)(C_3H_7)(NaSO_3)OH + NaCl.$$

This compound is of particular interest, as it proves beyond a doubt that diazo compounds, derived from the higher homologues of aniline, can be combined in the same way as diazobenzole, with thymole sulpho-acid, to form compound azo dye-stuffs.

From the foregoing we might naturally be led to expect that diazoxylole and diazo-naphthalene can, in like manner, be combined with alpha thymole sulpho-acid. The verification of this assumption will be detailed in the following experiment :

Azoxylole alpha thymole sulpho-acid,

$$C_6H_3(CH_3)_2 — N = N — C_6H(CH_3)(C_3H_7)(HSO_3)OH.$$

This compound is produced by dissolving 6.1 grms. of xylidine in 11 grms. of strong HCl, diluted with 100 c.c. of water. To this is then added, under constant stirring, 4.2 grms. of KNO_2, previously dissolved in 50 c.c. of water.

The diazo-xylole chloride thus formed is poured, little by little, into a solution consisting of 17.3 grms. of the soda salt of alpha thymole sulpho-acid, dissolved in 100 c.c. of water, rendered alkaline with 4 grms. of KOH.

A copious brown precipitate of the soda salt is thus formed. This was then collected on a filter, washed several times, and then dissolved in boiling water. The solution so obtained was then filtered, in order to separate it from a tarry residue which was formed while dissolving with boiling water. The filtrate, when cold, coagulates into a thick, slimy mixture, and as this failed to crystallize, one-half of it was then treated with a concentrated solution of $BaCl_2$.

This immediately threw down a copious, yellow-brown precipitate of the barium salt. It was then washed several times with water, in order to remove all traces of $BaCl_2$, and then dissolved in boiling alcohol, and allowed to cool.

Barium Salt.

$$[C_6H_3(CH_3)_2 - N = N - C_6H(CH_3)(C_3H_7)(OH)SO_3]_2Ba.$$

This salt is obtained, as already described, from the soda salt, by treating with $BaCl_2$.

It is insoluble in cold, and very nearly insoluble in boiling water. It is, however, quite soluble in hot 90 per cent. alcohol, from which it crystallizes in two forms. By rapid evaporation of the hot alcoholic solution, the barium salt is deposited, as a network of hair-fine, yellow needles. By slow evaporation, on the contrary, pretty lemon-yellow leaflets are obtained.

This salt should contain the following percentage of barium :

THEORY.

Barium.................................15.92 per cent.

FOUND.

Barium.................................15.42 per cent.

Free Acid.

$$C_6H_3(CH_3)_2 - N = N - C_6H(CH_3)(C_3H_7)(HSO_3)OH.$$

This compound was obtained by treating the second half of the slimy soda salt with an excess of strong HCl, which threw it down as a copious red-brown precipitate.

This was then collected on a filter, and washed with cold water till the excess of HCl had been removed, and was then treated with boiling water, in which it is but sparingly soluble.

The hot solution was then filtered, in order to separate it from a tarry residue, and the filtrate allowed to cool. When cold, the free acid separates out in little, yellow, hair-fine needles, which were cooled on a filter, washed and dried.

Boiling water acts upon this compound in the same manner as the two previously described bodies ; that is, there is partial decomposition, with evolution of gas bubbles (probably nitrogen), and formation of a tarry residue which smells very much like xylenole.

Therefore, from what we have seen, the unstability of these compounds might lead us to assume that the azo radical ($-N=N-$) is only very loosely bound to the benzole nucleus in thymole sulpho-acid, and that, consequently, the mere boiling with water is sufficient to loosen the bonds between them, at the same time giving off nitrogen, and forming the corresponding phenole.

Should this be the case, the decomposition referred to might be expressed as follows:

$$C_6H_3(CH_3)_2 - N = N - C_6H(CH_3)(C_3H_7)(HSO_3)OH) + (H_2O =$$
$$C_6H_3(CH_3)_2OH + C_6H_2(CH_3)(C_3H_7)(HSO_3)OH) + (N_2.$$

Compounds of this nature might be looked upon as belonging to the diazo group ; but, even were this assumed, I hardly think that the mere splitting up of the molecule (as above indicated) in these substances, is sufficient proof to classify them among the diazo compounds.

Diazo compounds are, as is well known, subject to a large number of transformations, of which the above reaction is one. But setting this one aside, I cannot find among my new substances any other characterizing features which should justify me in putting them under the head of diazo compounds ; and I must, therefore, look upon them as highly unstable compound azo bodies.

It will likewise be observed here, that the solubility of these substances decreases as the molecular weight rises, a fact which might have a tendency to explain their increased unstability.

Another curious fact may be mentioned here, namely, that these substances have all the same yellow shade of color, whereas the dyestuffs derived from phenole and naphthole usually increase in depth of shade as the molecular weight rises.

For the above reason it was, therefore, not considered worth the while to try the action of diazonaphthalene on thymole sulpho-acid, as it might be supposed that the compound resulting from such a reaction would be too unstable to investigate, or that there might be no compound found whatsoever.

Therefore, to sum up, it will be seen that thymole sulpho-acid can be combined with diazo compounds, but that the resulting substances increase in unstability as their molecular weight rises.