

Here the vapor-pressures of the hypobromite solution are seen to be considerably less than the pressures of pure water. The effect of *different concentrations* of hypobromite may be seen in the following table :

NaBr Solution	H <sub>2</sub> O added	Specific Gravity	Vapor Pressure	Difference H <sub>2</sub> O
I	0	1.253	10.70	9.56
I	1	1.131	12.77	7.49
I	3	1.052	15.75	4.53
I	7	1.033	17.50	2.76
I	∞	1.000	20.26	0.00

In the preceding table, (p. 1318) cubic centimeters of oxygen under various conditions of temperature and pressure are calculated to milligrams of hydrogen peroxide, corrections for the aqueous pressure of the hypobromite (sp. gr. 1.25) and the effect of temperature on the barometric column are included.

By the use of this new gasometer, this hypobromite method and the table for calculating, the determination of hydrogen peroxide is made not only rapid and accurate but the necessity of preparing and correcting standard solutions is avoided and the presence of the usual preservatives in the peroxide solution can be neglected.

URBANA, ILL.  
June 14th, 1907.

## THE ACTION OF PHOSPHORUS OXYCHLORIDE ON 1,8-NAPHTHYLAMINE SULPHONIC ACID.

BY FREDERIC DANNERTH.

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As early as the year 1887 Schultz made short mention of an inner-anhydrid of 1,8-naphthol-sulphonic acid which he had prepared for the first time by heating this latter compound with concentrated sulphuric acid. The pure product appears as colorless difficultly soluble prisms having a melting point of 154°. Because of its similarity to the lactones he named the new substance Naphtsultone. Our knowledge of the lactone of hydroxy-benzoic acid and the lactam of amino-benzoic acid suggests at once the possibility of an amino derivative similar to this naph-t-sultone. Dressel and Kothe in their researches on the sulphonation of naphthalene derivatives succeeded in preparing compounds of this type.

On treating 1,8-naphthylaminesulphonic acid with concentrated sulphuric acid and heating, they obtained a body which according to the analysis and its chemical behavior seemed to be a sulphonic acid of an inner-anhydrid, which they then called naphtsultam. Unfortunately this anhydrid formation was always accompanied by sulphonation in the nucleus so that it at that time appeared impossible to obtain the pure mother-substance. Bearing this in mind an attempt was made to remove the molecule of water with a reagent which would leave the nucleus in-



droxides is due to the formation of metallic salts. The "imino" group has assumed an acid nature due to the influence of the negative  $\text{SO}_2$  group. The sodium salt was prepared by treating the alcoholic solution of the naphtsultam with dilute sodium hydroxide. Beautiful yellow crystals separate and may be recrystallized from dilute alcohol. The salt was dried at  $150^\circ$  and analyzed.

Analysis :

$\text{C}_{10}\text{H}_8\text{O}_2\text{NSNa}$  (227.19)

Calculated : 10.15 per cent. Na

Found : 10.28

Naphtsultam forms with the alkaline earths difficultly soluble yellow compounds. From all these salts the naphtsultam may be recovered by acidifying with dilute hydrochloric acid. Below are given some of the reactions of the new body :

$\text{K}_2\text{Cr}_2\text{O}_7$  : gives a dark blue flocculent precipitate with the sultam in acetic acid solution.

$\text{FeCl}_3$  : gives with alcoholic solution of the sultam a dark blue precipitate.

Amyl nitrite : 4.1 grams of naphtsultam were dissolved in alcohol acidified with hydrochloric acid and then treated with 2.35 grams of amyl nitrite. After warming a few minutes and then cooling a red crystalline body separates.

The sodium salt of naphtsultam yields dyes when coupled with diazo-bodies.

O-diamino-toluene gives a violet dye.

$\beta$ -naphthylamine gives a blue dye.

*$\omega$ -Methyl Naphtsultam.* 2 grams of naphtsultam were heated to  $100^\circ$  in a Carius tube for four hours with four grams of methyl iodide and 0.4 grams of sodium. On removing the tube the new compound could be seen in the form of laminated crystals. After recrystallization from methyl alcohol it showed a melting point of  $125^\circ$ . The compound is easily soluble in alcohol with green fluorescence.

Analysis :

$\text{C}_{11}\text{H}_9\text{O}_2\text{NS}$  (219.16)

Calculated C = 60.23 H = 4.13 N = 6.40

Found 60.07 4.19 6.41

*Ethyl Naphtsultam.* This compound was prepared in a manner analogous to the methyl derivative. The contents of the Carius tube were poured into cold water, and the precipitated ethyl derivative recrystallized from ethyl alcohol. The alcoholic solution exhibits an emerald green fluorescence. (M.P.  $85^\circ$ ).

Analysis :

$C_{11}H_{11}O_2NS$  (233.18)

Calculated : 6.02 per cent. N

Found : 6.12

*1-Methyl-Naphthylamine-8-Sulphonic Acid.* As a means of proving the identity of methyl naphthylamine this latter compound was saponified. If the methyl group is linked to the nitrogen atom, the melt should yield the above mentioned sulphonic acid; if on the other hand the methyl group is linked to an oxygen atom the saponification will yield an amino-sulphonic acid which will be capable of diazotization. The absence of an amino group in the present case was proved by the fact that the compound would absorb no nitrous acid.

*Preparation :* In a small Erlenmeyer flask two grams of potassium hydroxide were heated with a few drops of water and about one gram of methyl naphthylamine introduced. The substance melts, is saponified and falls to the bottom as an insoluble white mass. The excess of potash solution is poured off and the difficultly soluble potassium salt is boiled with a large amount of water, filtered, acidified with hydrochloric acid and allowed to cool slowly. The gray crystals which separate are filtered off, washed with alcohol and recrystallized from boiling water. They possess no melting point. This compound is especially interesting as Fussganger in his attempts at preparing it by direct methods always obtained the dimethyl derivative.

Analysis :

Found : C = 55.28 H = 5.03 N = 6.02 S = 13.15 per cent.

Calculated for methyl naphthylamine sulphonic acid ( $C_{11}H_{11}O_2NS$ ) 237.18

C = 55.65 H = 4.67 N = 5.92 S = 13.52 per cent.

Calculated for naphthylamine sulphonic acid ( $C_{10}H_9O_2NS$ ) 223.17

C = 53.76 H = 4.06 N = 6.29 S = 14.36 per cent.

*Di-Brom-Naphtsultam.* The action of bromine on naphthylamine seems to vary with the form in which this substance is allowed to act. Bromine water brominates first and then exercises an oxidizing action. The addition of the first few drops causes the precipitation of a white granular body which soon changes color passing from pale green to dark blue. Pure bromine on being added drop by drop to the acetic acid solution of naphthylamine causes the precipitation of the white dibromide, which after recrystallization from chloroform had a melting point of  $239^\circ$ . The raw product turns a dark blue on boiling with alcohol.

Analysis :

$C_{10}H_7O_2NS$  (363.0)

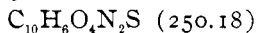
Calculated : 44.05 per cent. Br

Found : 43.82

*Mono-Nitro-Naphtsultam.* In order to obtain this body it was neces-

sary to prevent the formation of higher nitro bodies by using dilute nitric acid. One gram of naphtsultam was treated with a mixture of 5 cc. nitric acid, (sp. gr. 1.4) and 5 cc. of water. The white sultam gradually assumes a yellow color. After completion of the reaction it is filtered off and recrystallized from glacial acetic acid plus acetone. Melting point of the crystals  $253^{\circ}$ .

Analysis :



Calculated : 11.2 per cent. N

Found : 11.31

*2,4-Dinitro-Naphtsultam.* By the action of concentrated nitric acid (sp. gr. 1.45) two nitro groups can be introduced into the nucleus of the sultam. Two grams of dry naphtsultam were treated in a small Erlenmeyer flask with excess of nitric acid. The evolution of nitrogen oxides takes place immediately. After a few minutes a few small particles of ice are placed in the flask, whereby the nitro body separates out. On recrystallization from alcohol beautiful six-sided prisms containing acetone of crystallization are obtained. The crystals melt at  $259^{\circ}$  and then decompose. In order to determine the position of the nitro groups the 2,4-disulphonic acid of the sultam was made use of. The sulphonic groups were replaced by nitro groups according to the method of Dressel and Kothe.

40 grams of the sodium salt of naphtsultam 2,4-disulphonic acid were mixed in the cold with 200 grams of concentrated sulphuric acid. The mixture was cooled and then 40 grams concentrated sulphuric acid plus 22 grams of nitric acid (1.4) were added. The temperature should not rise above  $20^{\circ}$ . After all the acid has been added the mixture is heated to about  $35^{\circ}$  in order to complete the reaction. It is now poured on chipped ice and the body which separates is recrystallized from acetone. The melting point, reactions and analysis showed that this compound was identical with the original.

Analysis :



Calculated : 14.27 per cent. N

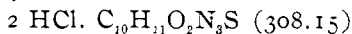
Found : 14.17

*2,4-Diamino-Naphtsultam.* Although it was impossible to prepare this compound, owing to its rapid oxidation and ready solubility, the hydrochloride was obtained with comparative ease.

In a small Erlenmeyer flask five grams of stannous chloride and 10 cc. of concentrated hydrochloric acid were heated and one gram of dinitro naphtsultam was introduced. After heating slightly the reaction sets in and soon all goes into solution; on cooling, the dihydrochloride is obtained

crystallizing from hot dilute alcohol quickly undergo oxidation when moist, thereby assuming a red color. The salt was dried in a vacuum dessicator over caustic potash.

Analysis :



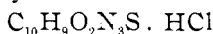
Calculated : 23.04 per cent. Cl

Found : 22.9

The pure diamine is readily decomposed. The salts crystallize well, are soluble in water, difficultly soluble in dilute hydrochloric acid. Ferric chloride colors the aqueous solution a deep wine red. Although this is a diamine the characteristic "Bismarck brown" coloration is not obtained with nitrous acid owing to the fact that both the ortho and para positions to the amino group are occupied. On coupling the diazo compound with a naphthol a red-brown dye is obtained. On boiling the aqueous solution of the diamine hydrochloride the liquid becomes turbid but on cooling, beautiful black crystals insoluble in water are deposited.

On mixing the diamine hydrochloride with a small quantity of water it at first dissolves but is soon precipitated in the form of deep-yellow crystals. On recrystallizing from boiling water they were obtained pure and proved to be the mono-hydrochloride.

Analysis :



Calculated : 13.06 per cent. Cl

Found : 13.28

*2,4-Di-Acetyl-Diamino-Naphtsultam.* In order to better characterize the diamine just obtained, its acetyl derivative was prepared. Anhydrous sodium acetate was heated with freshly distilled acetic anhydride and the diamine added. The acetyl derivative soon separates as a greenish-yellow body. After washing on the filter plate with water, acetic acid, alcohol and ether it was recrystallized from nitrobenzene. Small needles having a melting point of  $290^\circ$  were obtained.

*Iso-Naphtsultam.* On attempting to acetylate the naphtsultam a body was obtained which on analysis gave figures corresponding to the normal naphtsultam. The structural formula of this latter compound at once suggested that a rearrangement of the atoms had taken place, which would be a very interesting case of Desmotropism. That this was the case was proven by several reactions.

*Preparations of the Iso-Body :* 2 grams of naphtsultam were treated with two grams of boiling acetic anhydride for  $\frac{3}{4}$  of an hour in a small Erlenmeyer flask equipped with a condenser tube. Toward the end of the reaction beautiful rhombic crystals separate whereupon all is poured into a beaker of water in order to remove the excess of acetic anhydride. On recrystallizing from boiling alcohol crystals having a melting point of

188° are obtained. The crystals are soluble in chloroform, acetic acid and benzene.

Analysis :

$C_{10}H_7O_2NS$  (205.15)

Calculated : C = 58.49 H = 3.44 N = 6.84

Found : 59.29 3.83 6.96

Although the carbon value is slightly high, the molecular weight determination by the freezing point method gave good results.

Benzene constant = 50.

0.1650 g. dissolved in 15.94 g. benzene. Dep. = 0.255°

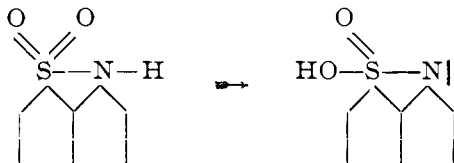
Molecular weight calculated : 205.2

found : 203.0

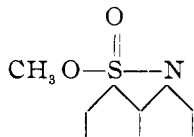
0.1320 g. dissolved in 22.73 g. benzene. Dep. = 0.140°

found : 207.0

These figures indicate sufficiently that a union of two molecules did not take place, but that the atoms had suffered a rearrangement according to the formula :



The iso-naphtsultam is soluble in boiling 50 per cent. sodium hydroxide with the formation of a yellow sodium salt. On acidifying this solution a white precipitate of the normal naphtsultam is obtained. An unsuccessful attempt was made to prepare the silver salt in order to obtain the methoxy derivative :



The usual method of introducing alkyl groups by heating in a Carius tube, as also the method with diethyl sulphate, yielded no results. The main difficulty seems to lie in the instability of the iso-body, in the presence of alkalis. The attempt to prepare the methyl ether by leading hydrochloric acid gas into the mixture of dry methyl alcohol and iso-naphtsultam for four hours resulted in the formation of a chlorine derivative, which is soluble in alcohol. The solution was evaporated and the substance recrystallized from dilute alcohol. The crystals have a melting point of 200°-201°.

Analysis :

$C_{10}H_8O_2NSCl$  (239.5)

Calculated : 14.80 per cent.

Found : 14.67

A chlorine derivative having the identical melting point was obtained by leading chlorine into the ice cold solution of iso-naphtsultam for thirty minutes. The substance left on evaporating the solution was recrystallized from a mixture of alcohol and chloroform. The conditions under which this latter body was obtained indicate that the chlorine had entered the nucleus.

Phosphorus pentachloride reacts with iso-naphtsultam at 188°. The melt is a mixture of oxidized bodies soluble partly in ether, in alcohol and in benzene. The ethereal solution gave a small yield of perfect hexagonal crystals not sufficient for an analysis.

*Mono-Brom-Iso-naphtsultam.* To the chloroform solution of the iso-naphtsultam bromine was added until the solution assumed a permanent yellow color. The white crystalline body obtained on evaporation when recrystallized from glacial acetic acid had a melting point of 162°. The color of the impure compound is changed to blue on boiling with dilute acetic acid.

Analysis :

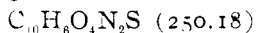


Calculated : 11.2 per cent. N 11.29 per cent. S

Found : 27.98 11.32

*Mono-Nitro-Iso-naphtsultam.* One gram of the iso-naphtsultam was treated with an equal weight of nitric acid (sp. gr. = 1.4) in a flask. At first no action is perceptible. On warming slightly the iso-naphtsultam is dissolved with great evolution of heat and on cooling pale yellow crystals are obtained, which when recrystallized from acetic acid show a melting point of 212°.

Analysis :



Calculated : 11.2 per cent. N

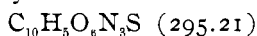
Found : 11.3

The body is soluble in a 10 per cent. solution of sodium hydroxide forming an orange-red salt. On acidifying a yellow precipitate is obtained, which on recrystallization melts at 252°, indicating a reversion to the normal compound.

*2,4-Dinitro-Iso-naphtsultam.* Fuming nitric acid reacts violently with the iso-body, the reaction being accompanied with a great evolution of heat. The solution deposits yellow crystals which when purified with acetone melt at 256°. If the reaction is not allowed to proceed far enough, the mono-nitro body is obtained. On the other hand the extended action of the hot acid results in the formation of an infusible body. If too much acid has been used the nitro-body will not precipitate on cooling. In this case it can be salted out by adding a solution of caustic soda, taking care that the solution retains a slight acidity.



Analysis :



Calculated : 14.27 per cent. N

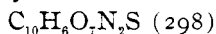
Found : 14.31

On heating this substance with sodium hydroxide and then acidifying the normal dinitro naphsultam is obtained.

*2,4-Dinitro-Naphthalene-8-Sulphonic Acid.* If the iso-naphsultam is heated with an excess of fuming nitric acid, an almost clear solution is obtained. When cool this is filtered with an asbestos filter. The filtrate is almost neutralized with a concentrated solution of potassium hydroxide avoiding at the same time any great increase in temperature. On cooling, the crystals separate and are recrystallized from boiling water. On heating the substance on a platinum foil it does not melt but explodes at about 300°. The yellow solution in sodium carbonate yields large crystals of the sodium salt.

The same sulphonic acid was prepared from the "normal" naphsultam as also from the naphsultam-2,4-disulphonic acid on treating these latter compounds with hot fuming nitric acid. This may be taken as proof of the position of the nitro groups. On recrystallizing from hot water, needles two centimeters in length may be obtained.

Analysis :



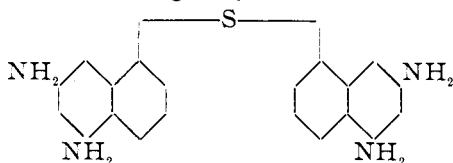
Calculated : C 40.26 per cent. N 9.39 per cent.

Found : 40.2 9.66

*2,4-Diamino-Naphthalene-8-Sulphonic Acid.*— One gram of the nitro compound just described was placed in a mixture of 4.5 g. stannous chloride and 15 cc. of concentrated hydrochloride acid. At first a deep red color is produced but on heating all dissolves to a yellow solution. On cooling the flask and contents the hydrochloride separates and may be dried in a desiccator over caustic potash. A further proof of the position of the nitro groups in the preceding compound was the "Bismarck brown" coloration obtained with nitrous acid. Therefore also the position "1" must be unoccupied, otherwise the two molecules could not unite. On moistening the hydrochloride with alcohol or with dilute caustic soda it assumes a blue color. On boiling the aqueous solution and subsequent cooling beautiful black needles are obtained; these possess no melting point.

Oxidation with  $\text{PbO}_2$  yields a coloring matter which dyes wool a violet color in acid solution. Vigorous reduction with a boiling mixture of stannous chloride and hydrochloric acid yields a different product. The nitro body is changed in color to a dark brown with evolution of hydrogen sulphide, and the product of the reaction behaves altogether different from the diamine just described. Possibly the sulphonic acid

group has been reduced to a mercaptan and then with the elimination of hydrogen sulphide the following body was obtained.



In conclusion I wish to thank Professor L. Gattermann for valuable assistance and Professor Carl Duisberg for his kindness in supplying large quantities of raw materials for the experiments.

Germantown, Philadelphia

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE  
UNIVERSITY OF ILLINOIS].

### AN IMPROVED METHOD FOR THE PREPARATION OF ALKYL CHLORIDES.

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On account of the variety of reactions into which they enter, the alkyl halides and their preparation are of especial interest and importance. Though quite satisfactory methods for the preparation of the bromides and iodides are in common use, the present methods used for preparing the corresponding chlorides are open to serious objections, principally on account of the smallness of yields. The necessity of preparing considerable quantities of a number of higher alkyl chlorides for another line of research led us to investigate more closely the methods hitherto employed, in order to determine the best conditions and methods for the preparation of these compounds.

The first alkyl chloride was prepared in 1759 by Rouelle, who treated ethyl alcohol with the chlorides of sulphur, antimony, tin, iron, bismuth, and aluminum respectively. In 1801 Basse prepared the same chloride by treating alcohol with gaseous hydrochloric acid and,<sup>1</sup> modified by the addition of zinc chloride<sup>2</sup> in the case of methyl and ethyl alcohols and by heating in sealed tubes the higher alcohols saturated with gaseous hydrochloric acid, this remained the favorite method for many years.

In 1871 Pierre and Puchot,<sup>3</sup> working with propyl and butyl alcohols, discarded the reactions in sealed tubes, in favor of the reaction of phosphorus pentachloride with alcohols<sup>4</sup>, and this method of preparation, to-

<sup>1</sup> Balard, *Ann.* 52, 312; Zincke, *Ann.* 152, 4; Rossi, *Ann.* 159, 72; Cross, *Ann.* 189, 3; Butlerow, *Ann.* 189, 51; Rohn, *Ann.* 190, 312; Brocket, *Ann.* 77 10, 384; Kaschirsky, *Russ. Ber.* 13, 90.

<sup>2</sup> Groves, *Ann.* 174, 372. Krüger *J. pr. Chem.* (2) 14, 195.

<sup>3</sup> *Ann.* 163, 265.

<sup>4</sup> Cahours, *Ann.* 37, 164; Borris, *Ann.* 92, 398; Limpricht, *Ann.* 103, 81; Butlerow, *Ann.* 177, 183; Pieverling, *Ann.* 183, 348; Winogradow, *Ann.* 191, 131; Wysznegradsky, *Ann.* 190, 336; Saytzen, *Ann.* 179, 321; Butlerow, *Bull. soc. chim.* 5, 24; LeBel, *Bull. soc. chim.* 25, 546; Henry, *Bull. soc. chim.* 41, 363; Mourgues, *Ber.* 23, 658; Fawosky, *Russ. Ber.*, 19, 425; Grigorowitsch, Pawlow, *Russ. Ber.* 23, 166.