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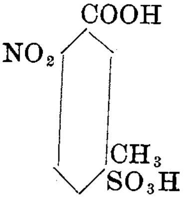
THE 4-NITRO-5-METHYL-2-SULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

WILLIAM J. KARSLAKE AND PERRY A. BOND.

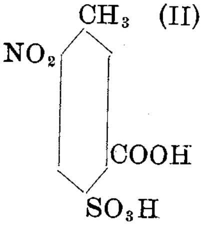
The 4-nitro-5-methyl-2-sulphobenzoic acid has been investigated to a limited extent as one of the products formed when the 6-nitro-1, 3-dimethyl-4-sulphonic acid is oxidized by potassium permanganate in dilute alkaline solution. Previous to this research,[1] the only record of its preparation was by Limpricht,[2] in which case only a small amount of the neutral potassium salt was isolated. He gives this as occurring with one-half a molecule of water of crystallization, but does not state which of the two methyl groups of the original acid had been oxidized. The neutral potassium salt does not seem to contain any water of crystallization, however, and some doubt is cast upon the value of the observation as made by him.

Since the preparation of our acid is intimately associated with the work of Karslake and Bond upon the oxidation of the 6-nitro-1, 3-dimethyl-4-sulphonic acid, it seems best to outline the work already done. This is the more necessary, as since the publication of the results of that work it has been found that the materials were not absolutely pure, and that certain irregularities occurring as a result of this fact may be explained and corrected in the new work. It may be said here, however, that in no case does this error affect the final conclusions which were drawn at that time.

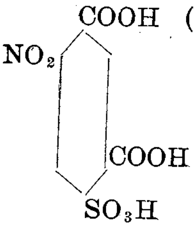
When 6-nitro-1, 3-dimethyl-4-sulphonic acid is oxidized in very dilute potassium hydroxide solution, three main products are formed. These are the salts of the 6-nitro-3-methyl-4-sulphobenzoic acid (I), the 4-nitro-5-methyl-2-sulphobenzoic acid (II), and the 6-nitro-4-sulphoisophthalic acid (III).



(I)



(II)



(III)

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[1] Karslake and Bond, J. Am. Chem. Soc., 31, 405, 1909.
[2] Limpricht, Ber., 18, 2191, 1885.

As has been shown by Remsen,[3] List and Stein,[4] and others, the ortho sulphobenzoic acids either substituted or unsubstituted, give two isomeric acid chlorides, while such isomers are not found in case the carboxylic and sulphonic acid groups are in the meta or para position with respect to one another. In this instance it was found that on treatment with phosphorous pentachloride, the three salts of the acids which had been isolated from one another behaved differently, one of the dibasic acids giving only one acid chloride, while the isomeric acid gave two acid chlorides. The tribasic acid gave two chlorides also, as would be expected from the theory.

The original investigation of these acids was carried only far enough to establish their constitution. The analyses of the products covered a few salts of each, and the presence or absence of the isomeric acid chlorides was confirmed by the preparation of the ammonia derivatives. None of the products were analyzed, their differentiation being by means of their melting points and crystalline form.

Later, Karslake and Huston[5] made derivatives of the 6-nitro-3-methyl-4-sulphobenzoic acid. They confirmed the presence of only one acid chloride not only directly, but also through the appearance of a single series of derivatives including the amide, anilide, toluide, and diester, in which nothing was found that would indicate that the acid chloride as made could be other than a simple substance. The present work was undertaken to complete our knowledge of the second of these three acids.

In previous work by Karslake and Bond,[6] the 4-nitro-5-methyl-2-sulphobenzoic acid was obtained in the form of the neutral potassium salt as the first crop of crystals from the oxidized nitro-xylene sulphonic acid. Analyses of this salt were persistently low in potassium, as is shown by the reported 20.96 per cent potassium as against the calculated 23.21 per cent. Analyses of the barium, acid barium, and silver salts gave very close results, however, and the constitution of the acid was considered fixed in spite of the discrepancy in the values for the potassium salt. Since then it has been found that this first crop of crystals is usually contaminated with unoxidized 6-nitro-1, 3-dimethyl-4-sulphonic acid in the form of the potassium salt.

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[3] Am. Chem. J., 30, 247, 1903.
[4] Ber., 31, 1648, 1898.
[5] J. Am. Chem. Soc., 31, 1057, 1909.
[6] Loc. cit.

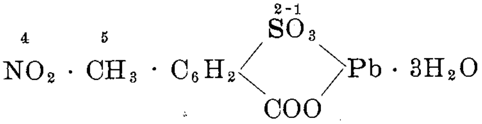
The separation was accomplished finally by systematic fractional crystallization, the crystals being filtered off first from the fairly concentrated solution at 50°, and then from the cold, somewhat diluted filtrate after standing several hours. The products thus obtained were recrystallized with due attention to temperature and concentration, until a complete separation was effected. Two criteria were used in determining purity. First, the salt of the original xylene sulphonic acid crystallized in needles, the complete absence of which under the microscope indicated purity; second, it was found that while the unoxidized nitro-xylene sulphonic acid salt has a very intense bitter sweet taste, the pure oxidized substance has practically none, what little can be perceived being only that characteristic of the potassium ion. This latter test is more delicate than the first and was used largely in determining the purity of a given fraction. About one hundred separate crystallizations were made in the purifying of the 235 grams of the potassium salt used as a basis for this research. The influence of the impurity has very definite effects, and its removal was a necessity, as will be seen especially in the preparation of the acid chlorides. Analyses of the purified potassium salt, while slightly low, are much better than before.

.1678 g. potassium salt gave .0859 g. K_2SO_4.
.1560 g. potassium salt gave .0800 g. K_2SO_4.

Theory for $C_8H_5O_7NSK_2$	Found
Potassium, 23.21 per cent.	22.95 - 23.01 per cent.

The neutral barium salt was prepared and analyzed previously, as was also the neutral silver salt. Neither contain water of crystallization. The acid barium salt crystallizes with two molecules of water. In addition to the foregoing, we have prepared the acid potassium salt and the lead salt.

Neutral Lead Salt.



$$\overset{4}{NO_2} \cdot \overset{5}{CH_3} \cdot C_6H_2\left\langle\begin{matrix}\overset{2-1}{SO_3}\\ COO\end{matrix}\right\rangle Pb \cdot 3H_2O$$

This salt was made by adding slightly more than the calculated amount of $Pb(NO_3)_2$ to the water solution of the potassium salt. It crystallizes quickly from moderately concentrated solution in fine crystals, which in some cases form leaf-like groups. Lead was determined by direct ignition in the crucible as the sulphate.

.2000 g. of the lead salt gave .0200 g. water and .1154 g. $PbSO_4$.

Theory for $C_8H_5O_7NSPb \cdot 3H_2O$	Found
Water, 10.38 per cent.	10.00 per cent.
Lead, 39.8 per cent.	39.45 per cent.

Acid Potassium Salt.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot \overset{2}{S}O_3K \cdot \overset{1}{C}OOH \cdot H_2O$$

This salt has been prepared in two ways; either by precipitating the silver from the silver potassium salt by dilute hydrochloric acid, evaporating and crystallizing; or by recrystallizing the neutral potassium salt from very concentrated hydrochloric acid. In the latter case, unless the hydrochloric acid is strong in the solution, the neutral potassium salt crystallizes out again, probably on account of its lesser solubility in water. The acid potassium salt once formed, however, can be recrystallized from water without decomposition. It comes out of the solution in beautiful fine needles containing one molecule of water of crystallization.

.1863 g. potassium acid salt gave .0107 H_2O and .0490 g. K_2SO_4.
.2258 g. potassium acid salt gave .0600 g. K_2SO_4.
.3061 g. potassium acid salt neutralized 8.9 cc. .10676N NaOH.

Theory for $C_8H_6O_7NSK \cdot H_2O$		Found
Water,	5.67 per cent.	5.74 per cent.
Acid hydrogen,	0.315 per cent.	0.317 per cent.
Potassium,	12.33 per cent.	11.81 - 11.92 per cent.

The Free Acid.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot \overset{2}{S}O_3H \cdot \overset{1}{C}OOH \cdot 3H_2O$$

The free acid was prepared from the pure neutral silver salt by adding just a trifle more than the calculated amount of 0.1 N hydrochloric acid to the water solution of the salt, boiling, filtering, and evaporating to a small volume. The acid crystallized from water in platelike needles strongly rosetted and easily broken. It had only a slight yellowish tint. It was insoluble in ether, ligroin, and carbon tetrachloride. It was soluble in acetone, ethyl acetate, or glacial acetic acid. Its melting point when it was crystallized from acetone or alcohol was

94°. The acid was titrated with sodium hydroxide, using phenolphthalein as the indicator.

.1916 g. acid gave .0330 H_2O and required 5.60 cc .1088N HCl for its neutralization in the Kjeldahl process.

.2057 g. acid required 11.90 cc. .1088N NaOH for direct neutralization.

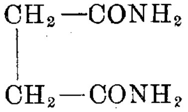
Theory for $C_8H_7O_7NS.3H_2O$		Found
Water,	17.14 per cent.	17.22 per cent.
Acid hydrogen,	.635 per cent.	.626 per cent.
Nitrogen,	4.44 per cent.	4.45 per cent.

The Acid Chlorides.

When the potassium salt of the 4-nitro-5-methyl-2-sulphobenzoic acid is heated with phosphorous pentachloride, it is converted into the acid chloride. The product is not a simple substance. On crystallizing from carbon tetrachloride, it gives two characteristically different crystalline forms which have the same composition, but which differ materially in respect to their behavior with certain reagents such as ammonia, aniline, etc. The appearance of these isomeric chlorides is characteristic of the ortho acids either of the ortho dicarboxylic or ortho sulphobenzoic type. It is among the latter especially that the problem has been worked upon,[7] since the dicarboxylic acids, e. g., ortho phthalic acids, have a tendency to form a large excess of one isomer and very little of the other.

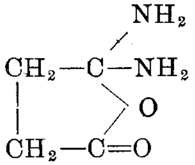
The original argument regarding the constitution of these acid chlorides was based probably on the work done by Auger[8] on the chlorides of the dibasic acids. He found that if succinyl chloride was treated with ammonia, it gave a different diamine than when the ester of succinic acid was acted upon, and, since the latter could not have a symmetrical formula (I), he assigned to the isomeric body the formula (II). The ease with which the symmetrical diamine goes over into the imine (III) is comparable with that of the formation of the acid anhydride, and forms part of the argument.

I



$$\begin{array}{l} CH_2-CONH_2 \\ | \\ CH_2-CONH_2 \end{array}$$

II



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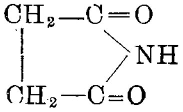

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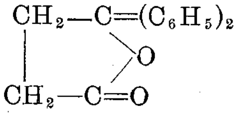
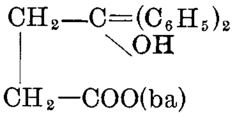
[7] Remsen and Students, Am. Chem. J., 30, 247, 1903.
[8] Auger. Bl. 39, 346, 1888.

Auger also points out that when the succinyl chloride is treated with benzene and aluminium chloride, it gives two products, mainly, however, one, to which he gives the unsymmetrical formula (IV) on the ground that when saponified with barium hydroxide, it gives not the original succinic acid, but a diphenyl derivative, a monobasic acid, which may be formulated (V), while the isomeric product, which may be ten per cent of the total, is not acted upon.

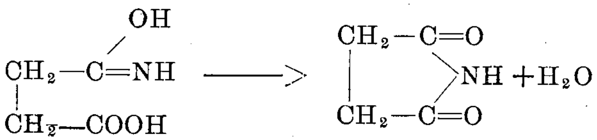
IV



V



The analogy is carried to the phthalic acids which, according to Auger, occur only in the unsymmetrical form. D. Vörlander[9] has objected to the idea of isomeric chlorides. He explains the action of the imine on the basis of the formation of an isomer of an amido acid.



He objects to any form of reasoning through the use of the acid chloride with benzene where a substance like aluminium chloride is involved in the reaction. However, the isolation of the ortho sulphobenzoic acid chlorides in two forms as carried on by Remsen and his pupils, has put an end to any doubt which there may have been regarding the existence of two separate distinct acid chlorides in such cases, and has strongly reflected credit on the work of Auger. We shall use the terms symmetrical and unsymmetrical in the same sense in which he used them.

It was formerly stated[10] that the treatment of the potassium salt of the 4-nitro-5-methyl-2-sulphobenzoic acid with phosphorous pentachloride in a flask with reflux condenser at boiling temperature produced an oily substance which solidified with difficulty, but on being dissolved in carbon tetrachloride, dried, and partly evaporated, gave two products, one melting at 133°, the other an oily substance for which a melting point of 93° was suggested. It had been the experience of others that the

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[9] Ber., 30, 2268, 1897.
[10] Loc. cit. (Karslake and Bond.)

low melting and high melting chlorides crystallized in a constant melting mixture which had a lower melting point than that of the low melting chloride. The two were separated in these cases by distilling in a vacuum.

The formerly observed melting point for the high melting chloride is approximately correct, the new value adopted being 134°, but now it has been definitely shown that the low melting point acid chloride melts at 83°, and is not involved as the prime cause of the oily mixture. In this case, as distinguished from the experience of others, no oil was produced when pure initial potassium salt was used, the two chlorides crystallizing out in absolutely distinct crystalline form. They were separated by fractional crystallization, and the symmetrical, high melting chloride showed a tendency toward the formation of supersaturated solutions in carbon tetrachloride, the solvent used for the purification. The oily mass formerly found by Karslake and Bond was, however, reproduced by mixing with the low melting acid chloride, a portion of the acid chloride of the unoxidized nitro-xylene sulphonic acid. Its source in that work was evidently the impurity mentioned at the beginning of this paper.

Symmetrical Acid Chloride.

$$\overset{4}{NO_2} \cdot \overset{5}{CH_3} \cdot C_6H_2 \cdot \overset{2}{SO_2}Cl \cdot \overset{1}{CO}Cl$$

The symmetrical acid chloride was formed in the largest amounts when the potassium salt of the acid was treated with phosphorous pentachloride in an open dish at the temperature of the steam bath, the ratio of the symmetrical to the unsymmetrical acid chloride thus formed being about three to five, and the total yield reaching seventy-five per cent of the theoretical.

When the heating had caused complete liquifaction of the mass in the open dish, it was removed from the steam bath and poured into cold water. Phosphorous oxychloride and any phosphorous pentachloride remaining were dissolved in the water, and after a time the oil hardened. It was broken up with a stirring rod and ground with fresh water in a mortar. Finally the powder was let stand in more water over night, filtered, and the solid dried over sulphuric acid in a dessicator. It was next dissolved in hot carbon tetrachloride, filtered, and let stand to crystallize. If the solution was concentrated, the unsymmetrical chloride crystallized first and later there were superimposed on the crystalline mass hard, glistening, rhombohedral crystals of the symmetrical chloride. These were picked out by hand from the mass. In another experiment it was found that this chloride crystallized in the form of long white needles. Once these were produced in the laboratory, the rhombohedral forms never appeared again. The needles seemed to be less soluble than the unsymmetrical acid chloride, and hence could be taken out from the carbon tetrachloride solution as the first crop of crystals. In some cases the solution was seeded to bring about the rapid production of this form.

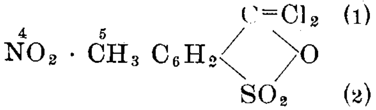
The identity of the two crystalline forms of the symmetrical acid chloride was shown by the identical melting points, 134°, and also by the fact that when the rhombohedral form was dissolved in carbon tetrachloride and a trace of the needles added, the whole amount present crystallized out in the needle form.

The symmetrical acid chloride was recrystallized from carbon tetrachloride several times until the melting point was constant at 134°, and then was analyzed. Chlorine was determined by saponifying with sodium hydroxide, acidifying with nitric acid, and precipitating as silver chloride. Sulphur was determined by Pringsheim's method using sodium peroxide; nitrogen was determined by the Gunning method.

.1569 g. chloride gave .1500 g. silver chloride.
.1278 g. chloride gave .1241 g. silver chloride.
.1264 g. chloride gave .0896 g. barium sulphate.
.3140 g. chloride required 9.68 cc of .1084N HCl.
.2973 g. chloride required 9.08 cc of .1084N HCl.

Theory for $C_8H_5O_5NSCl_2$		Found
Chlorine,	23.80 per cent.	23.65 - 24 02 per cent.
Nitrogen,	4.70 per cent.	4.68 - 4.64 per cent.
Sulphur,	10.74 per cent.	10.72 per cent.

Unsymmetrical Acid Chloride.



$$\overset{4}{\mathrm{NO_2}} \cdot \overset{5}{\mathrm{CH_3}}\ \mathrm{C_6H_2}\left\langle \begin{matrix} \mathrm{C{=}Cl_2}\ (1) \\ \mathrm{SO_2}\ (2) \end{matrix} \right\rangle \mathrm{O}$$

This acid chloride constituted about five-eighths of the total yield of the acid chlorides as made by the open dish method. Its formation is apparently favored by the presence of phosphorous oxychloride, for when a reflux condenser is used in the preparation of the chlorides, and the condensed phosphorous oxychloride formed is kept in the mixture, a much larger per cent of the unsymmetrical chloride is produced, although the absolute yield seems to be smaller. Holmes[11] used phosphorous oxychloride in sealed tubes for the preparation of the pure unsymmetrical acid chloride of p-nitro-o-sulphobenzoic acid. In this case we found it not necessary, and the shorter process was used.

The purification of the unsymmetrical acid chloride by fractional crystallization from carbon tetrachloride was not difficult. It crystallized in short, tufted, rather soft needles, yellowish in color. An attempt was made to use the method of List and Stein[12] for the purification of the acid chlorides by distillation in vacuo. It was expected that the symmetrical chloride would decompose at the distillation temperature, while the unsymmetrical would distil unchanged. Distillation took place at the following temperatures and pressures.

Pressure in mm. mercury	Boiling point
21	218 - 220°
11	214°
10	212°

It was found that both acid chlorides distilled unchanged under these conditions. The distillation mixture was composed of nearly pure 83° melting chloride; no attempt was made to distil the 134° melting acid chloride either alone or when there was any large per cent of it in the mixture. No difference was made in the melting point of the pure 83° melting point substance, though its color was nearly destroyed by the distillation.

The acid chloride melting at 83° was analyzed, the methods used being the same as in the case of the high melting chloride.

.3849 g. acid chloride gave .3626 g. silver chloride.
.3848 g. acid chloride gave .3646 g. silver chloride.
.2780 g. acid chloride gave .2636 g. silver chloride.
.2780 g. acid chloride gave .2180 g. barium sulphate.
.2869 g. acid chloride required 9.06 cc 1084N HCl.
.1823 g. acid chloride required 5.80 cc 1084N HCl.

Theory for $C_8H_5O_5NSCl_2$	Found
Chlorine, 23.80 per cent.	23.3 - 23.40 - 23.46 per cent.
Nitrogen, 4.70 per cent.	4.82 - 4.79 per cent.
Sulphur, 10.74 per cent.	10.77 per cent.

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[11] Am. Chem. J., 25, 204, 1901.
[12] Ber., 31, 1648, 1898.

The slightly low values shown for chlorine are due probably to the presence of some acid in the acid chloride. In all its reactions this form of the chloride seems more labile than the symmetrical form, and while the decomposition is very slow by water or heat, yet it seems to take place to a definite degree. It will be noted that the values for nitrogen or sulphur would be almost unaffected by the transformation of a small amount of the acid chloride into the acid, what little difference might be produced being according to the indications of the analysis.

Some Other Attempts to Make the Acid Chlorides.

Since the use of phosphorous pentachloride is attended by the production of the fumes of phosphorous oxychloride, and also as the yield of the acid chlorides made by that method is not as large as might be desired, an attempt was made to use sulphuryl chloride for their preparation. An attempt was made on the potassium salt of the 6-nitro-3-methyl-4-sulphobenzoic acid, which forms the chloride more easily than the acid which we were investigating. Four grams of the material were mixed with about 3 grams of the SO_2Cl_2, and the mixture heated with the use of a reflux condenser for several hours. On pouring into water, it solidified at once, but when an attempt was made to crystallize from carbon tetrachloride it refused to dissolve, showing that the acid chloride, which is easily soluble, had not been formed. The product slowly dissolved in water. The acid chloride apparently could not be formed in this way.

Since chlorsulphonic acid has a higher boiling point than the sulphuryl chloride, an attempt was made to use it as in the preceding case. Four grams of the potassium salt of the 6-nitro-3-methyl-4-sulphobenzoic acid were treated with the calculated amount of chlorsulphonic acid, and heated with the use of a reflux condenser. The material melted and gases were given off, the action apparently being vigorous. On pouring into water and filtering the residue, only a very small amount of the acid chloride seemed to have been formed.

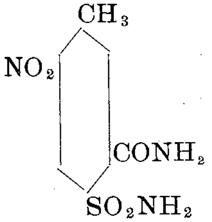
Another attempt was made by using twice the theoretical amount of the chlorsulphonic acid, heating on the steam bath, and dropping more carefully into cold water so as to prevent hydrolysis. The oily precipitate solidified and settled over night. When this was filtered and washed, the yield was about twenty-five per cent of that demanded by the theory. On recrystallizing from carbon tetrachloride, it gave a melting point of 90° which corresponds to the acid chloride of this acid.

While the use of the chlorsulphonic acid is of moderate value for the preparation as given above, it has been found that in the case of the isomeric 4-nitro-5-methyl-2-sulphobenzoic acid in which we are interested, the yield approaches zero. The change which is produced in this case runs almost wholly along the line of the production of a soluble crystalline substance which is formed as a by-product in the making of the acid chlorides by all the methods tried. This body was not investigated. A few analyses showed that it probably was neither the acid nor the acid potassium salt.

DERIVATIVES OBTAINED BY THE ACTION OF AMMONIA ON THE ACID CHLORIDES.

A. *From the Symmetrical Acid Chloride.*—The symmetrical acid chloride is only slightly acted upon in nonaqueous solutions by ammonia, but when treated with strong aqueous ammonia, the pure chloride may be dissolved at boiling temperature with the formation of a substance soluble in water which might be either the diamide (I), or the ammonium salt of the imide (II).

I



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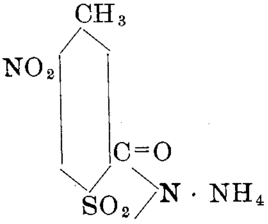
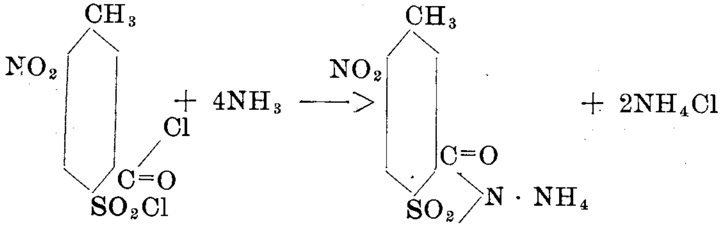
II



The product is the latter, since it can be formed from the imide by simple neutralization with ammonia, also because when its solution is treated with sodium hydroxide as in the Kjeldahl method and the mixture distilled, the presence of one and only one ammonium group is shown. The passage from the o-diamide to the ammonium salt, moreover, would be very easy under the conditions of the experiment. No other substance was recovered in the preparation, excepting, of course, the ammonium chloride formed in the reaction.



A suitable amount of the acid chloride was placed in an open beaker and treated with concentrated ammonia. Apparently there was no action in the cold, but on raising the temperature slowly to boiling, so as to keep the concentration of the ammonia as high as possible, the acid chloride dissolved. When the excess of ammonia was evaporated off and the residue was cooled somewhat, the ammonium salt of the imide crystallized out as small glistening cubes. These were recrystallized from water several times. They then gave a melting point, with decomposition, of 310°-320°.

Total nitrogen was determined by the modified Gunning method, and sulphur by the Liebig method. Ammoniacal nitrogen was determined by dissolving a weighed portion of the salt in water in a Kjeldahl flask, adding 30 cc. of strong sodium hydroxide, and distilling into .1N hydrochloric acid.

.2193 g. ammonium salt required 23.41 cc .1084N hydrochloric acid.

.1950 g. ammonium salt required 20.80 cc .1084N hydrochloric acid.

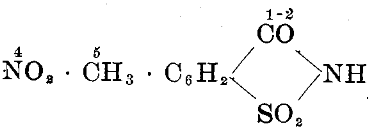
For ammoniacal nitrogen—

.3002 g. ammonium salt required 11.00 cc .1088N hydrochloric acid.

.1674 g. ammonium salt gave .1509 g. barium sulphate.

	Theory for $C_8H_9O_5N_3S$	Found
Total nitrogen,	16.21 per cent.	16.20 - 16.18 per cent.
Ammon. nitrogen,	5.40 per cent.	5.58 per cent.
Sulphur,	12.35 per cent.	12.38 per cent.

The Imide.



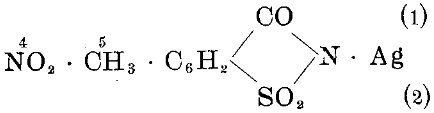
$$\overset{4}{NO_2} \cdot \overset{5}{CH_3} \cdot C_6H_2 \left\langle \begin{matrix} \overset{1-2}{CO} \\ SO_2 \end{matrix} \right\rangle NH$$

When the cold mother liquor from the crystallization of the ammonium salt of the imide is made acid with hydrochloric acid, the imide separates almost quantitatively from the solution. At slightly elevated temperatures it is more soluble so that it comes out in a nice crystalline condition. It is colorless, and the crystals as viewed under the microscope are platelike needles, so thin in one dimension that the edge appears only as a line under a magnification of 150 diameters. The insolubility of the precipitate makes it unnecessary to purify except by washing with water until free from chlorides. The imide is bitter tasting. It is readily soluble in alkali, as would be expected from the presence of the imide group. It forms salts with various metals, by which it may be characterized more completely. Its melting point is 213.5°. The methods of analysis were those used for the ammonium salt.

.1168 g. imide required 9.00 cc .1084N HCl.
.1156 g. imide required 8.97 cc .1084N HCl.
.1643 g. imide gave .1584 g. barium sulphate.

	Theory for $C_8H_6O_5N_2S$	Found
Nitrogen,	11.57 per cent.	11.77 - 11.68 per cent.
Sulphur,	13.22 per cent.	13.25 per cent.

Silver Salt of the Imide.



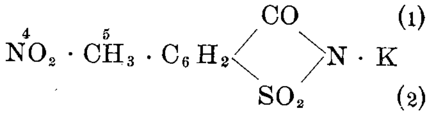
$$\overset{4}{NO_2} \cdot \overset{5}{CH_3} \cdot C_6H_2 \begin{matrix} CO \\ SO_2 \end{matrix} N \cdot Ag \quad \begin{matrix} (1) \\ (2) \end{matrix}$$

When the imide was dissolved in a large volume of hot water, and a solution of silver nitrate added, a white crystalline precipitate slowly appeared. The crystals were platelike needles, somewhat rosetted, but these rosettes were very loosely held together and easily broke up into the long, thin, square ended needles. The salt contained no water of crystallization. It was less soluble than the silver salt of the cyan acid to be described later. The determination of silver was made by charring the salt in a porcelain crucible with sulphurc acid, and reducing the silver sulphate directly in the same container. This seemed to give better results than attempting to precipitate the silver as the chloride from a litre or more of solution. Some difficulty was encountered in the heating, however, as the silver salt decomposed suddenly and the loss by the puffing from the crucible spoiled the analysis, unless the rate of charring was carefully regulated.

.1173 g. silver salt gave .0362 g. silver.

Theory for $C_8H_5O_5N_2S.Ag$	Found
Silver, 30.92 per cent.	30.87 per cent.

Potassium Salt of the Imide.



The potassium salt of the imide, which is much more soluble than either the silver salt or the original imide, is made by treating the ammonium salt of the imide in hot, quite concentrated solution with an excess of strong potassium carbonate. An immediate crystalline precipitate appears, which may come down more slowly from more dilute solution. It can be recrystallized from water as there is considerable difference between its solubility in hot and cold water. The mother liquors and wash waters if acidified give the free imide, and in this way the material may be saved. The potassium salt crystallizes in peculiar shaped plates, which are sometimes rosetted together, but often occur separately.

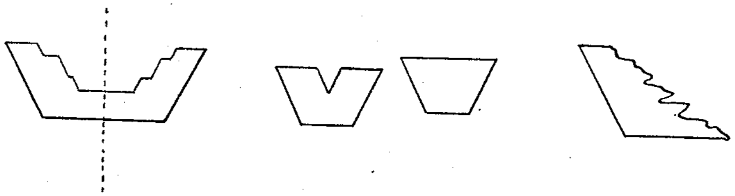


FIG. 7.

The figures given, figure 7, excepting the last one, are all double, as the rosetting, when such occurs, takes place at the middle of the figures shown above, ie., along the dotted line. The second crystallization gave a solution free from alkali. It has a weak bitter taste. There is no water of crystallization. Potassium was determined as potassium sulphate in the manner described for the silver salt.

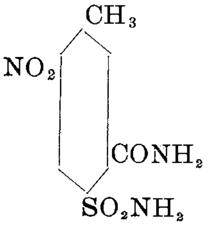
.1610 g. potassium salt imide gave .0499 g. potassium sulphate.

Theory for $C_8H_5O_5N_2S.K$	Found
Potassium, 13.96 per cent.	13.91 per cent.

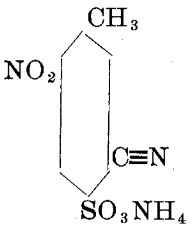
B. From the Unsymmetrical Chloride.—If the acid chloride melting at 83° is treated with cold concentrated ammonia, an action takes place which while beginning slowly, at last goes on rapidly with the evolution of heat. The behavior in this respect is characteristically different from that of the symmetrical chloride. In making the ammonia derivative in practice, the ammonia was diluted with three parts of water to lessen the action. If the ammonia is evaporated off and the remaining liquid is concentrated and cooled, crystals form in nodules. These crystals are not as sharply defined as those of the corresponding ammonium salt of the imide; the nodules appear to be made up of compact masses of radiating crystals which branch continually into fanlike shapes. When these nodules are crushed, it is impossible to find any characteristic crystalline form. Recrystallized from alcohol, however, the crystals were not bunched but seemed to be laminated plates almost cubical in form, but with no smooth surfaces. The yield of the product is good. In no case was there any indication of the ammonium salt of the imide. The salt is more soluble than the ammonium salt of the imide. Its melting point is 310-311°, with decomposition.

Since this salt is not the ammonium salt of the imide, it must be either the diamine (I), or the ammonium salt of the cyan acid (II).

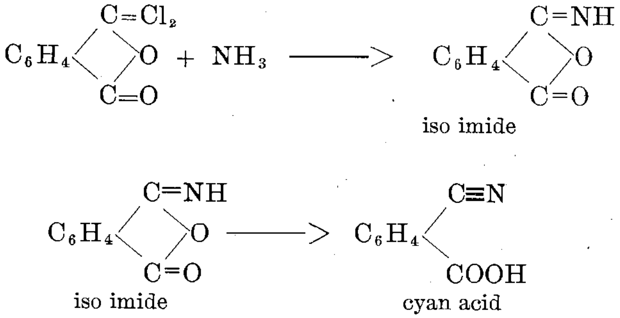
I



II



The cyan formula for bodies of this type is derived from the work of Hoogewerff and Van Dorp[13], on the action of ammonia on phthalic chloride. They give the reaction thus—



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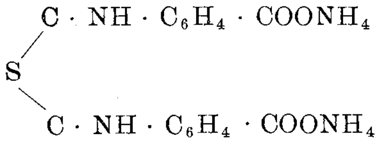
[13] Rec. Trav. Chim., 11, 84; 12, 12, 1892.

If this latter is treated with alcoholic ammonium sulphide, it gives



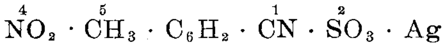
analogous to benzamide as made from benzonitrile and ammonium sulphide. This indicates the nitrile formula. That our compound is the cyan acid is also shown by its salts, which characterize it as a monobasic acid.

The ammonium salt has a very bitter taste. The free acid was not prepared. When hydrochloric acid is added to solutions of its salts, no precipitate appears. Analyses were made for nitrogen by the Gunning method, and for sulphur by Pringsheim's method.

.2966 g. ammonium salt required 31.19 cc .1084N HCl.
.1397 g. ammonium salt required 14.83 cc .1084N HCl.
.2801 g. ammonium salt gave 4 times .0623 and .067.

	Theory for $C_8H_9O_5N_3S$	Found
Nitrogen,	16.21 per cent.	16.11 - 15.95 per cent.
Sulphur,	12.35 per cent.	12.31 - 12.24 per cent.

Silver Salt of the Cyan Acid.



$$\overset{4}{NO_2} \cdot \overset{5}{CH_3} \cdot C_6H_2 \cdot \overset{1}{CN} \cdot \overset{2}{SO_3} \cdot Ag$$

The silver salt of the cyan acid was first prepared by adding silver nitrate solution to the hot solution of the ammonium salt. An attempt was then made to purify the precipitate by dissolving in much water, and letting it crystallize slowly. It was found, however, that decomposition was likely to take place when boiling the silver salt at high dilutions, and so the procedure was changed. The very dilute solution of the ammonium salt was heated, the silver nitrate solution was added only slightly in excess of the calculated amount, and the solution was cooled slowly. The silver salt precipitated in fairly heavy, pointed needles which were not clustered. When washed with cold water, they were ready for analysis. The drying should take place in the dark if a pure white product is obtained. The silver salt of the cyan acid is somewhat more soluble than the silver salt of the imide, but is still quite insoluble at ordinary temperatures. There is no water of crystallization. Silver was determined directly.

.2100 g. silver salt gave .0647 g. silver.

Theory for $C_8H_5O_5N_2S \cdot Ag$	Found
Silver, 30.92 per cent.	30.81 per cent.

Potassium Salt of the Cyan Acid.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot \overset{1}{C}N \cdot \overset{2}{S}O_3K$$

The potassium salt of the cyan acid was made by dissolving two grams of the ammonium salt in thirty-five cubic centimeters of water, and adding while hot one gram of potassium carbonate in ten cubic centimeters of water. The solution was boiled to drive off the ammonia at least partly, and then allowed to cool. The potassium salt crystallized out in clustered crystalline plates similar to figure 8, or sometimes in pairs resembling figure 9.

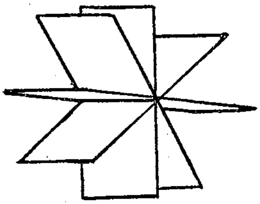


FIG. 8.

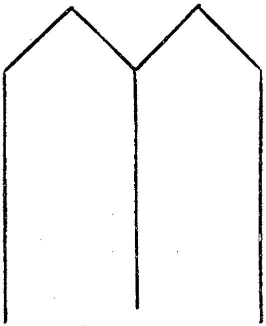


FIG. 9.

The salt was recrystallized from pure water. Its solubility is greater than that of the corresponding potassium salt of the imide. The taste is bitter in a degree corresponding to that of others of these compounds. The salt contained no water of crystallization. Potassium was determined as the sulphate.

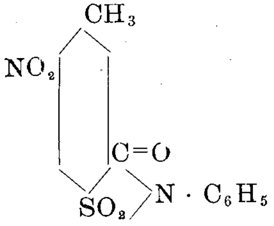
.1509 g. substance gave .0472 grams potassium sulphate.

Theory for $C_8H_5O_5N_2S \cdot K$	Found
Potassium, 13.96 per cent.	14.03 per cent.

DERIVATIVES OBTAINED BY THE ACTION OF ANILINE ON THE ACID CHLORIDES.

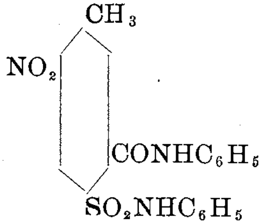
A. From the Symmetrical Chloride.—The formation of the anilids of the acid chlorides by previous experimenters in this field has been carried out in three ways: first, by the treatment of the solid acid chloride with aniline; second, by the treatment of the acid chloride with aniline in ether or chloroform solution; and third, by the action of aniline on the acid chloride in the presence of water. The first method has been found to be unsatisfactory. In general, the third method has been chosen by Remsen and his students[14] as it seemed to give the most constant results. In this work, however, it has been found that by using carbon tetrachloride as the solvent the products were of the same nature as those obtained by Remsen and his students by the water method. The process is shorter and the substances are easily separated from one another.

From the symmetrical acid chloride two products were obtained. One of these, which is insoluble in cold, reasonably dilute sodium hydroxide, is known as the anil. It corresponds to the formula

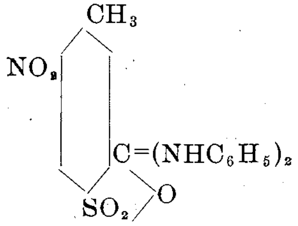


It resembles the imide in many respects, but does not form salts as it contains no imido hydrogen.

The other product contains two aniline residues and forms salts, ie., is easily soluble in dilute sodium hydroxide. For this the formula has been given as—



rather than—



The proof of these formulæ is given by analogy with that of the anil and symmetrical dianilid of o-sulphobenzoic acid. Remsen and Kohler[15] found that if the anil was boiled with sodium hydroxide solution it dissolved and could be precipitated again by acidifying the solution. It was not, however, the anil after this treatment, but an anilido acid, which could be transformed again into the anil by treating with phosphorous

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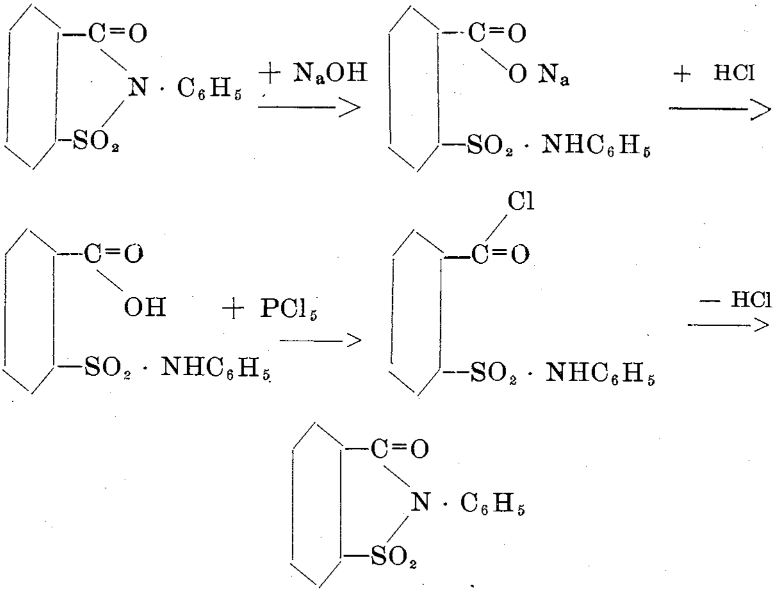
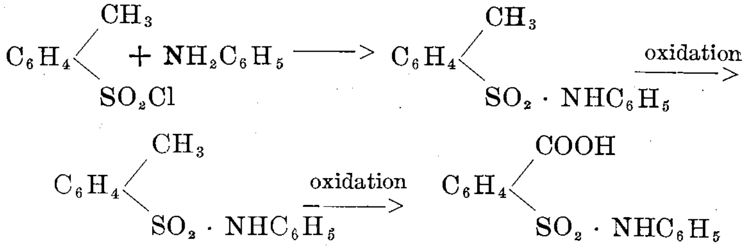
[14] Loc. cit.

[15] Am. Chem. J., 17, 338, 1895.

pentachloride in chloroform solution. The reactions may be represented as follows:



The structure of the anilido acid given above was shown synthetically by oxidizing with potassium permanganate the product obtained when o-toluene sulphonchloride was treated with aniline.



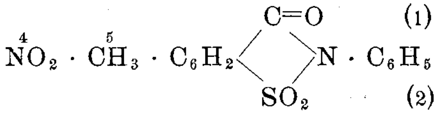
$$C_6H_4{<}\begin{matrix}CH_3\\SO_2Cl\end{matrix} + NH_2C_6H_5 \longrightarrow C_6H_4{<}\begin{matrix}CH_3\\SO_2\cdot NHC_6H_5\end{matrix} \xrightarrow{\text{oxidation}}$$

$$C_6H_4{<}\begin{matrix}CH_3\\SO_2\cdot NHC_6H_5\end{matrix} \xrightarrow{\text{oxidation}} C_6H_4{<}\begin{matrix}COOH\\SO_2\cdot NHC_6H_5\end{matrix}$$

The product made in this way is identical with that from the anil as mentioned above.

When the symmetrical anilide is boiled in alkaline solution, the first product is the salt of the anilido acid. If boiling is continued the neutral salt of the sulphobenzoic acid is formed. On account of the two steps in which the reaction takes place, Remsen and Kohler consider that the two anilido groups bear different relationships to the molecule. The reactions given would seem to indicate strongly the above presented structures for both the anil and the dianilide.

The Anil.



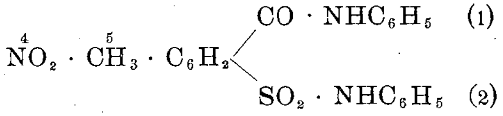
One gram of the symmetrical acid chloride was dissolved in about fifty cc of carbon tetrachloride at boiling temperature. While this was hot there was added aniline in excess of the amount calculated for the dianilide. This aniline also was dissolved in carbon tetrachloride, and the mixture was warmed for an hour. There was only a slight precipitate at the end of that time, hence the carbon tetrachloride was evaporated and the residue treated with dilute hydrochloric acid. After kneading the residue, which at this stage was oily in nature, for several minutes, the mass solidified. It was then broken up into fine fragments and was allowed to stand over night in order that the excess aniline might all dissolve as the hydrochloride. The residue was filtered, ground in a mortar with hydrochloric acid, filtered and washed with water to remove the excess of acid. It was next treated with cold, dilute potassium hydroxide. The solution became bright yellow, and a dirty white precipitate was left in an amount small as compared with the bulk of the original precipitate. This insoluble material, which was the anil, was washed with water, dried, and recrystallized from alcohol. The yield of crude anil was .27 gram.

The anil is very insoluble in alcohol except close to the boiling point. About one hundred cc of alcohol were required to recrystallize the anil as above. When pure, it is nearly white, and crystallizes in needles which have a melting point of 202-203°.

.1185 g. substance required 7.00 cc .1088N HCl.

Theory for $C_{14}H_{10}O_5N_2S$	Found
Nitrogen, 8.81 per cent.	9.00 per cent.

The Symmetrical Anilide.



The sodium hydroxide solution filtered from the anil was acidified with hydrochloric acid. A white curdy precipitate at once came down and was filtered off and washed free from acid. It was then redissolved and reprecipitated for further purification. Finally, it was washed, dried, and recrystallized from 75 per cent alcohol. It formed a fine cottony mass of soft needles with a melting point of 195°. The yield of the anilide was .98 gram. The substance was identified in this case not by analysis but by its exact correspondence with the dianilide formed under like conditions as a derivative of the unsymmetrical acid chloride. Mixtures of the two preparations showed the same melting point as that of either of the pure specimens.

List and Stein[16] state that there are three products formed by the action of aniline on the symmetrical chloride, but there was no indication of a third body here, and a consideration of the yields obtained will show that no very large amount of the material is unaccounted for.

.27 grams of anil is equivalent to	.25 grams of acid chloride.
.98 grams dianilide is equivalent to	.71 grams of acid chloride.
	.96
Amount of acid chloride taken	1.00

B. *From the Unsymmetrical Chloride.*—The process of making the derivatives of the unsymmetrical chloride was the same as that used in the action upon the symmetrical chloride. The unsymmetrical chloride was dissolved in carbon tetrachloride and to the hot solution was added aniline in carbon tetrachloride so long as the white precipitate—which in contradistinction to the action of the symmetrical chloride, came down on the first addition of aniline—continued to form. Hydrochloric acid vapor was evolved copiously, and the aniline hydrochloride apparently did not form to any great extent. There was required for the completion of the reaction a moderate excess above the two molecules of aniline to each molecule of the acid chloride. The precipitate which was thus formed, on being stirred gathered into a gummy mass which hardened as the solution cooled. Only a small amount of material was left in the carbon tetrachloride, but in order that all the products might be recovered, it was evaporated to dryness as before and the whole solid residue ground with hydrochloric acid in a mortar and then allowed to stand to remove soluble products. After some hours it was filtered and washed with a considerable amount of water. The washings were saved with the original filtrates. The precipi-

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[16] Loc. cit.

tate, which was insoluble in water was now treated with dilute sodium hydroxide in which it was almost completely soluble. Only a faint cloudiness remained in the solution, hence the conclusion was that nothing but the merest traces of anil could have been formed. The amount of anil produced from five grams of pure unsymmetrical acid chloride was only great enough to stain the filter paper. No positive identification of it was possible. This corresponds with the observation by Holmes[17] that no anil was produced from the unsymmetrical chloride of o-sulphobenzoic acid. From this solution the anilide was precipitated by hydrochloric acid as in the case of the symmetrical compound, washed, dried and recrystallized from alcohol. It was found in this case, however, that a large portion of the precipitated material would not dissolve even in hot alcohol. This substance, which proved to be the unsymmetrical anilide, will be described later.

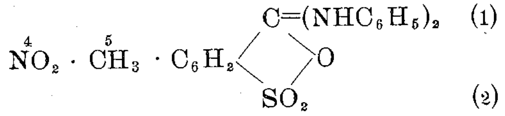
Symmetrical Anilide.

The alcohol solution mentioned above, on cooling gave a mass of soft needles which on recrystallization melted at 195°. This substance is identical with the anilide formed from the symmetrical chloride, and in conformity with the argument used in that case, is known as the symmetrical anilide. It is tasteless. The anilide was analyzed for sulphur by Pringsheim's method, and for nitrogen by the modified Gunning method.

.1461 g. substance required 9.78 cc .1084N HCl.
.1661 g. substance required 11.00 cc .1084N HCl.
.1775 g. substance gave .0255× 4 g. barium sulphate.

Theory for $C_{20}H_{17}O_5N_3S$		Found
Nitrogen,	10.22 per cent.	10.15 - 10.06 per cent.
Sulphur,	7.78 per cent.	7.91 per cent.

The Unsymmetrical Anilide.



$$\overset{4}{NO_2}\cdot\overset{5}{CH_3}\cdot C_6H_2\left\langle\begin{matrix}C{=}(NHC_6H_5)_2 & (1)\\ \quad >O & \\ SO_2 & (2)\end{matrix}\right.$$

The substance insoluble in alcohol was purified by dissolving in hot 75 per cent alcohol with the aid of sodium hydroxide added drop by drop until the precipitate had disappeared. To this solution acid was added, and the precipitate which formed after a delay of some seconds was nicely crystalline. The crystals

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[17] Am. Chem. J., 30, 275, 1903.

were very fine. The melting point seemed to be at 342°; but fusion did nót occur until after the product was quite black with heating. This behavior corresponds with that of the symmetrical anilides which have been described by others. The formula is given from the fact that it is formed only by the action of the unsymmetrical acid chloride, and also that the two anilido groups are intact in the compound.[18]

The unsymmetrical anilide is insoluble in most ordinary solvents and this is a general characteristic of such substances. Carbon tetrachloride, alcohol and benzene have little if any action on it. Analysis for sulphur was by Liebig's method and that for nitrogen by the modified Gunning method.

.1962 grams substance required 19.49 cc .1088N HCl.
.2187 grams substance gave .1237 grams barium sulphate.
.2253 grams substance gave .1261 grams barium sulphate.

	Theory for $C_{10}H_{17}O_5N_3S$	Found
Nitrogen,	10.22 per cent.	10.02 per cent.
Sulphur,	7.78 per cent.	7.77 - 7.69 per cent.

The third substance produced by the action of aniline on the unsymmetrical acid chloride is soluble in water, and was recovered by evaporating the filtrates from the various washings of the original dianilides. It crystallizes in clumps of needles whose fineness or coarseness is dependent on the rate of formation.

It is suspected that this body is the anilido acid, but it is not easy to purify and no very satisfactory analyses were obtained. It gives an acidity approaching that expected, but rather less, while it is high in nitrogen.

The total yields of the two anilides were almost equal, but the weight of the third body was less than either. This latter fact may be due to incomplete recovery, as the substance crystallized out in a fashion which showed it to have a solubility only slightly less than the sodium chloride with which it was mixed. It is also probable that there was considerable hydrolysis to the 4-nitro-5-methyl-2-sulphobenzoic acid. The total yield from a given amount of the acid chloride is not sufficient to account for all the material.

TRANSFORMATIONS OF THE ANILINE DERIVATIVES.

When either the symmetrical or unsymmetrical anilide is treated with phosphorous oxychloride, at boiling temperature,

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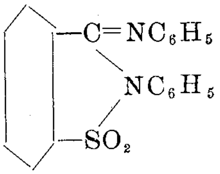
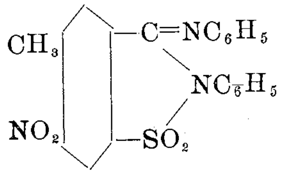
[18] Remsen and Hunter; Am. Chem. J., 18, 812, 1896.

for about one-half hour, a yellow colored solution is produced. If the excess of phosphorous oxychloride is distilled off with care, an air blast being used to help the process, a thick brownish oil is left, which after being cooled and treated with water to remove phosphoric acid, becomes a bright yellow powder. This powder is the dianil.

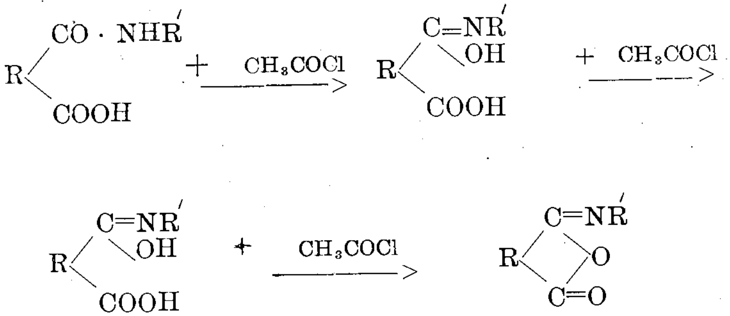
The dianil of o-sulphobenzoic acid was made and analyzed by Remsen and Hunter.[19] The formula assigned to the compound was—



corresponding to which we have



The basis of the formula is found in the work of several investigators. Hoogewerff and Van Dorp,[20] using phosphorous oxychloride or acetyl chloride, effected the formation of isoimides, by treating the amino derivatives of certain dibasic acids.



Jesurun[21] used practically the same reaction upon the ortho cyan benzene sulphone chloride, and obtained what appear to be analogous results.

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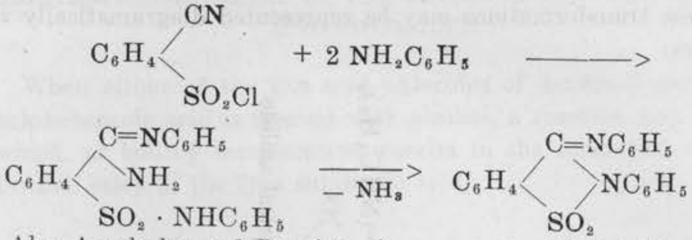
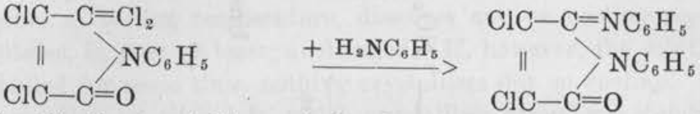
[19] Loc. cit.

[20] Loc. cit.

[21] Ber. 26, 2292, 1893.



Also Anschultz and Beavis[22] give a reaction of this kind for maleic dianil, which they form by the action of dichlor maleic anil on aniline.



The dianil recrystallizes nicely from acetone diluted with water, and forms short, bright yellow, hexagonal needles. It is soluble in other solvents, such as benzene and alcohol, and may be recrystallized from them if desired. The substance when recrystallized melts constantly at 188°. It was analyzed for nitrogen and sulphur.

.1793 g. substance requires 12.67 cc .1088N HCl.
.1950 g. substance gives .1150 g. barium sulphate.

	Theory for $C_{20}H_{15}O_4N_3S$	Found
Nitrogen,	10.69 per cent.	10.76 per cent.
Sulphur,	8.14 per cent.	8.10 per cent.

The anilides may be transformed into one another by various reagents. These processes have been worked out for various acids. Blanchard[23] worked with the anilides of p-brom sulphobenzoic acid, Henderson[24] and others with the corresponding p-nitro and unsubstituted bodies. The results in every case are similar to those given by the anilides herein described.

As has been stated, if either the unsymmetrical or symmetrical anilides are treated with phosphorous oxychloride we obtain the dianil. If the dianil is boiled with concentrated hydrochloric acid, it goes over into the colorless anil without dissolving, and the yellow color slowly disappears during the process. The melting point of the colorless solid, 202°, shows it to be the anil.

If the dianil is boiled for some time with glacial acetic acid until the solution, which is vivid yellow at first, becomes colorless, and the solution is allowed to stand, the unsymmetrical anilide crystallizes out. When washed with water and dried it has a melting point of approximately 342°, as described previously.

If the anil is warmed with aniline for some hours, and the excess of aniline distilled off with steam, the residue, when recrystallized from alcohol, proves to be the fusible or symmetrical anilide with a melting point of 195°.

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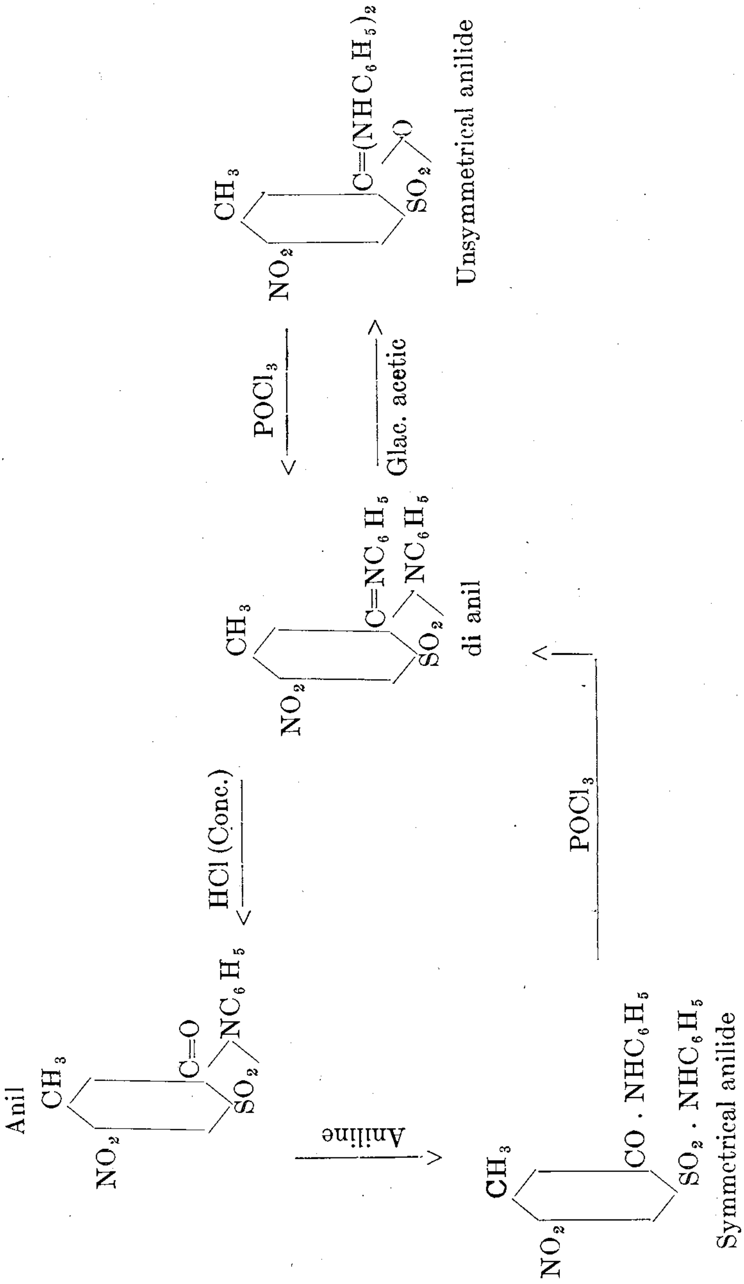
[22] Ber., 28, 58, 1895.
[23] Am. Chem. J., 30, 485, 1903.
[24] Am. Chem. J., 25, 1, 1901.

These transformations may be represented diagramatically as follows:



DERIVATIVES OBTAINED BY THE ACTION OF ALCOHOL ON THE ACID CHLORIDES.

When either of the two acid chlorides of 4-nitro-5-methyl-2-sulphobenzoic acid is treated with alcohol, a reaction may occur which, at boiling temperature, results in the formation of the benzoic ester of the free sulphonic acid,

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot CO\overset{1}{O}R \cdot SO_{\overset{2}{2}}OH$$

The symmetrical acid chloride on treatment with absolute alcohol at boiling temperature, dissolves and on cooling reprecipitates, in part at least, unchanged. If, however, the solution is boiled for some time, nothing crystallizes out on cooling. On evaporation an oil is left, which crystallizes after long standing as the alkyl ester of the free sulphonic acid mentioned above. There is no trace of chlorine in this product after recrystallization, hence the alkyl ester of the sulphone chloride appears not to be formed.

The unsymmetrical acid chloride goes into solution in alcohol rather easily even at ordinary temperatures. It was found best for purposes of obtaining the product, however, to dissolve the acid chloride at boiling temperature as in the other case. On cooling at once, there were deposited crystals which contained much chlorine, but which were not the original acid chloride. They were identified as the alkyl ester of the sulphone chloride,

$$\overset{5}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot CO\overset{1}{O}R \cdot SO_{\overset{2}{2}}Cl$$

The filtrate, on evaporation gave the same product as was obtained from the symmetrical chloride.

In work which has been done upon the acid chlorides of related bodies, such as the o-sulpho benzoic acid, by Sohon,[25] Henderson,[26] and Kastle,[27] or the p-nitro-o-sulpho benzoic acid by Chambers,[28] the results finally have been shown to be exactly like those obtained for our acid. Sohon and Kastle worked with impure substances, but the work of Henderson and Chambers is in complete agreement. Kastle's explanation of the process has

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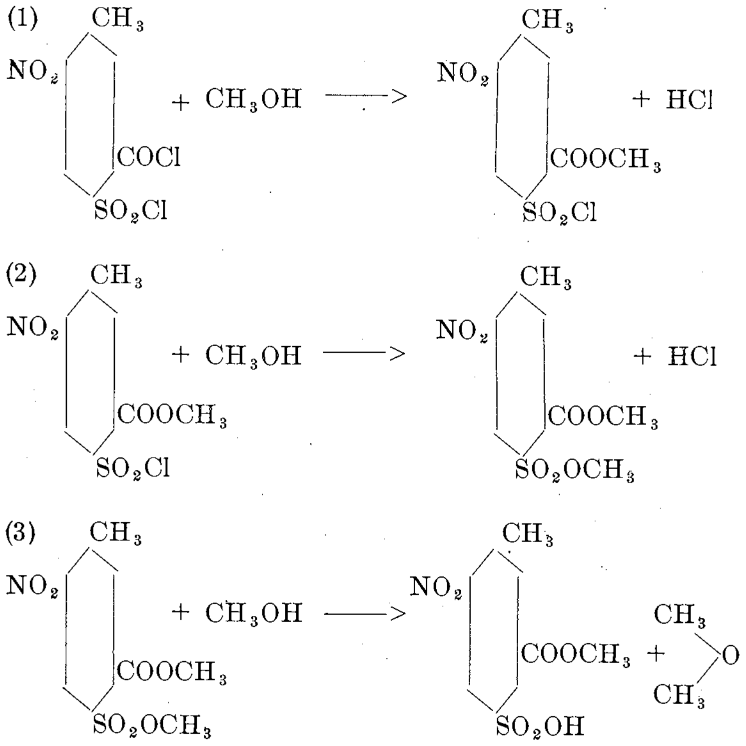
[25] Am. Chem. J., 20, 260, 1898.

[26] Am. Chem. J., 25, 8, 1901.

[27] Am. Chem. J., 11, 181, 1889.

[28] Am. Chem. J., 30, 387, 1903.

been adopted as the correct one. He states that the reaction proceeds in three steps according to which we would have,



Of the three substances formed, two, the first and third, are produced by boiling the unsymmetrical acid chloride with alcohol; only one, the third, is formed from the symmetrical chloride. The second product shown above has not been isolated in this reaction. It, the diester, has, however, been made in another way. Its instability toward hydrolizing agents will explain its easy decomposition, though in the absence of hydrochloric acid, it can be recrystallized from alcohol with only slight loss.

In all of the experiments with the alcoholic derivatives of the two acid chlorides, the final products are the same, the only difference being the formation of the ester of the sulphone chloride as an intermediate product in the action of the alcohol on the unsymmetrical acid chloride.

Methyl Ester Sulphone Chloride.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot C\overset{1}{O}OCH_3 \cdot S\overset{2}{O}_2Cl$$

This substance was prepared from the unsymmetrical acid chloride by dissolving in hot alcohol. The warming was kept up only long enough to obtain solution. When the solution was cooled, the sulphone chloride ester separated in long platelike crystals. It was washed with a very little absolute alcohol under suction and dried. It is very soluble in benzene, alcohol, acetone, ether and chloroform, and on this account a great deal of difficulty was encountered in purifying it. The solvent finally used was ligroin, in which the ester is not very soluble. Drying was by suction in a partial vacuum. After standing over night in a desiccator, the product, which has a melting point of 101°, was analyzed.

Chlorine was estimated by saponification with dilute potassium hydroxide in a small Erlenmeyer flask, then by exactly neutralizing with nitric acid, and finally by titrating with .1 N silver nitrate solution, using potassium chromate as the indicator. Sulphur was determined by the Liebig and nitrogen by the Gunning methods.

.2278 g. substance gave .1828 g. barium sulphate.
.1140 g. substance gave .0892 g. barium sulphate.
.2553 g. substance required 7.77 cc .1084N HCl.
.1985 g. substance required 6.09 cc .1084N HCl.
.1859 g. substance required 6.37 cc .1N Silver nitrate.
.2959 g. substance required 10.02 cc .1N Silver nitrate.

Theory for $C_9H_8O_6NSCl$		Found
Sulphur,	10.92 per cent.	10.75 - 11.02 per cent.
Nitrogen,	4.77 per cent.	4.66 - 4.61 per cent.
Chlorine,	12.08 per cent.	12.09 - 12.01 per cent.

Methyl Benzoic Ester of the Sulphonic Acid.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot C\overset{1}{O}OCH_3 \cdot S\overset{2}{O}_2OH$$

The methyl ester acid was prepared as described, by boiling either acid chloride with methyl alcohol for some time and evaporating to a syrup. On cooling it slowly formed crystals which on account of their extreme solubility were not purified. The identification was by means of the barium salt, which could be made easily. The silver salt, which was very soluble, was made but not analyzed. It was used in the preparation of the dimethyl ester.

For the preparation of the barium salt of the methyl ester acid, a portion of the syrupy solution of the acid was diluted slightly, and barium chloride added while the mixture was heated. When the mixture was cooled, long, fine, white needles arranged in well developed nodules crystallized out. They were recrystallized from dilute alcohol and barium was determined directly as the sulphate by ignition with sulphuric acid. There was no water of crystallization.

.2691 g. substance gave .0917 g. barium sulphate.

Theory for $C_{10}H_{10}O_6NSCl$	Found
Barium, 20.04 per cent.	20.05 per cent.

Ethyl Ester Sulphone Chloride.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_5 \cdot C_6H_2 \cdot C\overset{1}{O}OC_2H_5 \cdot S\overset{2}{O}_2Cl$$

The ethyl ester sulphone chloride was prepared exactly as the corresponding methyl compound had been prepared. Its properties are practically the same, and the appearance of the crystals, which are flat needles, is so nearly like that of the methyl ester chloride, that they cannot be distinguished under the microscope. The needles have characteristic ends, as illustrated in figure 10.

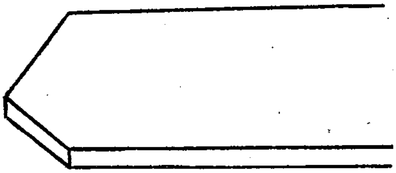


FIG. 10.

The melting point of the ethyl ester chloride is 72°, which seems peculiar, for the melting point of the methyl ester chloride is 101°.

The ester chloride was analyzed for nitrogen by the Gunning method, for sulphur by the Pringsheim method and for chlorine by saponifying, neutralizing with nitric acid, and titrating with silver nitrate solution.

.1748 g. substance required 5.04 cc .1084N HCl.
.1714 g. substance required 4.85 cc .1084N HCl.
.1463 g. substance gave 4×.0272 g. barium sulphate.
.2143 g. substance required 7.04 cc .1N Silver Nitrate.

Theory for $C_{10}H_{10}O_5NSCl$.		Found
Nitrogen,	4.55 per cent.	4.37 - 4.29 per cent.
Sulphur,	10.40 per cent.	10.21 per cent.
Chlorine,	11.54 per cent.	11.65 per cent.

Ethyl Benzoic Ester of the Sulphonic Acid.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot CO\overset{1}{O}C_2H_5 \cdot SO_2\overset{2}{O}H$$

This was made in the same manner as the methyl ester acid, and the free acid was not isolated, its presence being proven by the making and analysis of the barium salt. The salt crystallized in tufts of soft needles from the hot solution of the acid, to which barium chloride had been added. It was purified by recrystallizing from dilute alcohol.

.2244 g. substance gave .0742 g. barium sulphate.

Theory for $C_{10}H_{10}O_7NS.Ba$	Found
Barium, 19.26 per cent.	19.45 per cent.

The Dimethyl Ester.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot CO\overset{1}{O}CH_3 \cdot SO_2\overset{2}{O}CH_3$$

The dimethyl ester cannot be made by the direct action of the acid chlorides on alcohol. The method which seems to have been most commonly used (see Remsen and Bird,[29] or Cobb[30]) is the use of sodium methylate either dry or in absolute alcohol solution, with an absolute ether solution of the acid chloride. Cobb reports that the best yields are found when dry sodium methylate is added to the ether solution, but notes that in any case there is a tendency to pass over to the sodium salt of the ester acid, which is, of course, dissolved in the washing of the ether solution. This naturally affects the yield which can be obtained. This method was tried on both the symmetrical and unsymmetrical acid chlorides of our acid. It produced no satisfactory results. The pure acid chloride which melts at 134° gave no action which could be followed, when it was treated with dry sodium methylate in ether solution, though a pinkish color appeared as each portion of the methylate was added to the solution. The melting point of the substance recovered from the ether after treatment was 132°, and on analysis it gave 22.9 per cent chlorine as compared with the theoretical 23.5 per cent for the acid chloride. This indicates that in the main the acid chloride was unchanged.

The pure acid chloride which melts at 83° gave what was apparently a mixture of the unchanged acid chloride and the methyl ester chloride. The melting point of the product ranged

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[29] Am. Chem. J., 30, 262, 1903.
[30] Am. Chem. J., 35, 488, 1908.

from 60°, at which it softened, to 101°, at which the final melting occurred. An effort was made to use pyridine and alcohol on the ether solution of the acid chloride. It resulted in a good yield of the methyl ester sulphone chloride, melting nicely at 101°, but no dimethyl ester was formed.

Failing by the methods above given, recourse was had to Kastle's method of treating the dry silver salt of the methyl ester acid with methyl iodide. The silver salt of the methyl ester sulphonic acid was made by adding silver nitrate solution to the syrup obtained by boiling down a solution of the acid chloride in alcohol. It crystallized from the strong solution in cottony needles which were sucked dry and used without purification. The silver nitrate which was in excess would finally precipitate as silver iodide, and not interfere with the formation of the diester.

The salt was dried at 110° (it puffs at 140° unless quite pure) and was ground in a mortar. It was then placed in a pressure bottle and methyl iodide added in excess. Immediately a rapidly increasing yellow precipitate of silver iodide came down. The mixture was heated, however, at 100° under the pressure of its vapor in order to make sure of the completion of the reaction. The excess of the methyl iodide was then evaporated and the dry residue extracted with absolute ether and filtered. The product obtained by evaporating the ether was recrystallized from absolute methyl alcohol and it then gave a constant melting point of 94.5°. This melting point is remarkably close to that of the free 4-nitro-5-methyl-2-sulphobenzoic acid, but the substance is insoluble in water, and gives no acid reaction. It contains no chlorine, as was shown by hydrolyzing with potassium hydroxide and testing with silver nitrate. The diester was analyzed for nitrogen only, on account of the small amount of the material available.

.1869 grams substance required 6.12 cc .1088N HCl.

Theory for $C_{10}H_{11}O_7NS$	Found
Nitrogen, 4.85 per cent.	4.98 per cent.

DERIVATIVES OBTAINED BY THE ACTION OF PHENOL ON THE ACID CHLORIDES.

The action of phenol upon the acid chlorides offers no new facts bearing on the constitution of the latter. The products are of the same general nature as those given by the alcohols. Both acid chlorides seem to give practically the same derivatives.

Remsen and Saunders[31] made the phenol derivatives of o-sulphobenzoic acid by heating the high melting acid chloride with phenol. They obtained only the symmetrical diphenyl ester. Remsen and McKee[32] found that the unsymmetrical acid chloride gave the same results. More thorough work by Humphreys,[33] in which careful attention was paid to the temperature of the reaction, shows that at 40° the symmetrical acid chloride gives both the diphenyl ester and some of the phenyl ester sulphone chloride, while the unsymmetrical gives only the phenyl ester sulphone chloride; at 60° both acid chlorides give equal amounts of the above mentioned products; at 130° both acid chlorides give only the diphenyl ester. It would seem that the behavior is largely a function of the temperature, and that it is not safe to draw any general conclusions from the experimental data. Chambers[34] found that even at low temperatures the p-nitro-o-sulphobenzoic acid, when a very weak alkaline solution was used, as in the Schotten-Baumann reaction, gave the diphenyl ester.

In every instance noted, a water soluble red substance is also formed, probably a phthalein. No investigation has been made of it, and none was made here in spite of its evident presence. It is removed in the washing of the diphenyl ester with water. It shows the properties of an indicator. Alkalies, including ammonia, give a deep purple color, mineral acids a salmon pink solution. With acetic and tartaric acids, even in the presence of hydrochloric acids, the color is lemon yellow. However, excess of sulphuric acid prevents the development of the yellow color. The material for these tests was the unpurified substance obtained by heating phenol and the acid chloride together at a high temperature for some time. The difference in the behavior of the acids may be due to the presence of other substances than the phthalein proper.

Three methods were used in preparing the diphenyl ester. First, the acid chloride was warmed with phenol. The production of phthalein was so marked, that this method was used only for a trial preparation. The diester appears to be the only product outside of the phthalein.

Second, the Schotten-Baumann method was tried. The acid chloride was dissolved by gentle warming in a slight excess of

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[31] Am. Chem. J., 17, 353, 1895.
[32] Am. Chem. J., 18, 799, 1896.
[33] Am. Chem. J., 30, 292, 1903.
[34] Am. Chem. J., 30, 374, 1903.

phenol. When the solution was cooled, the yellow oil which formed was treated with an excess of dilute potassium hydroxide solution. There was instant reaction, though apparently no large amount of heat was developed. After being stirred for five minutes the oil solidified and was broken up with a stirring rod and allowed to stand. It was then filtered and washed with water. The amount of phthalein formed was small. On crystallizing from alcohol a melting point of 115° was obtained, but careful recrystallization from benzene, glacial acetic acid, and alcohol in order, gave a melting point of 123°. This identified it as the diphenyl ester, as will be shown later.

The third method is the one which was used practically for the preparation of the diphenyl ester for analysis. It consisted in treating the acid chloride with a mixture of pyridine and phenol. Two grams of phenol and an equal amount of pyridine were mixed in a small beaker and the powdered acid chloride added. At this point in the preparation occurred the only difference which was noticed between the action of the unsymmetrical and the symmetrical acid chlorides. The symmetrical acid chloride with the melting point of 134°, dissolved rapidly with the evolution of heat, while warming was neccessary in order that the unsymmetrical might react. The products were always the same, however, and the discussion of the method which follows will apply equally well to either acid chloride. It might be remarked that in all the chemical behavior of the two acid chorides this seems to be the only case when the high melting acid chloride is the more reactive. When the acid chloride had dissolved in the pyridine phenol solution the liquid was warmed for ten minutes on the water bath. This caused the formation of phthaleins, however, and in later preparations the warming was omitted, and instead the product simply was allowed to stand at room temperature for the completion of the reaction. Alcohol was then added and warmed until all the compound was in solution. As the liquid cooled crystals formed as colorless, flat needles somewhat resembling those of the ethyl benzoic ester of the sulphone chloride. These contained no chlorine, however, and were the diphenyl ester.

A scond crop of crystals which came down showed a canary yellow color. The crystal form was that of a blocky rhombohedron. The yellow color, it has been shown, while very persistent, is not characteristic, but due to the presence of phthalein dissolved in the crystal. Ordinary recrystallization does not remove the color. The crystals must be ground fine with water and allowed to stand with it for a long time in order to extract the phthalein. When this is done, they may be recrystallized from glacial acetic acid followed by alcohol, and are colorless, with a melting point of 206°. They contain no chlorine. These crystals were not formed in the Schotten-Baumann reaction. No sulphone chloride was formed by any of these three methods, a fact which was due in all probability to the temperature employed.

The Diphenyl Ester.

$$\overset{4}{N}O_2 \cdot \overset{5}{C}H_3 \cdot C_6H_2 \cdot \overset{1}{C}OOC_6H_5 \cdot SO_2\overset{2}{O}C_6H_5$$

The product melting at 123° which is formed in all of the preceding methods has been shown to be the diphenyl ester. The melting point of the crude product, is, according to our experience, always 115° or 116°, but by recrystallization from alcohol, benzene, alcohol, glacial acetic acid, and alcohol in the order named, the melting point becomes constant at 123°. The products which were obtained separately from the symmetrical and unsymmetrical acid chlorides, are identical in this respect as in all others. The pure substance was analyzed for nitrogen by the Gunning method, and for sulphur by the Liebig method.

.2066 g. substance required 4.65 cc .1088N HCl.
.2059 g. substance required 4.69 cc .1088N HCl.
.2023 g. substance gave .1144 g. barium sulphate.
.1631 g. substance gave .0933 g. barium sulphate.

Theory for $C_{20}H_{15}O_7NS$	Found
Nitrogen, 3.39 per cent.	3.42 - 3.47 per cent.
Sulphur, 7.75 per cent.	7.74 - 7.86 per cent.

The Product Melting at 206°.

The second product which was produced by the action of phenol in the presence of pyridine has not been identified positively. It gives the odor of pyridine on treatment with strong potassium hydroxide, and may be a pyridine salt of the phenyl benzoic ester of the sulphonic acid. Nitrogen, where pyridine groups are present, cannot be determined by any modification of the Kjeldahl method, as the results always are low, but the degree of loss in such case is fairly constant. If due allowance is made for this factor, the results vary only a few tenths of a per cent.

Theory for $\overset{4}{N}O_2 . \overset{5}{C}H_3 . C_6H_2 . CO\overset{1}{O}C_6H_5 . \overset{2}{S}O_3H . C_5H_5N$

		Found
Sulphur,	7.65 per cent.	7.69 per cent.
Nitrogen,	6.73 per cent.	5.91-5.99 per cent.

These figures cannot be called determinative. Lack of time prevented the determination of nitrogen by the absolute method.

CONCLUSIONS.

The writer cannot help feeling as a result of his study in this field, that the matter of the actual formulae of the two acid chlorides is still unsettled. It is true that the ammonia derivatives seem to give positive results, but when we come to the anilides, we find that the so-called symmetrical anilide is produced in equal quantity with the unsymmetrical anilide from the unsymmetrical acid chloride.

In the case of the alcoholic derivatives the differences in behavior are slight. The greater activity of the unsymmetrical acid chloride is manifest, and the formation of the sulphone chloride ester by it is different from the action of the symmetrical acid chloride which goes directly to the ester acid; but, as has been shown, the higher temperature required for the action of the symmetrical acid chloride on the alcohol would cause the hydrolysis of the ester of the sulphone chloride to give the ester of the sulphonic acid, just as it occurs on boiling the unsymmetrical acid chloride with alcohol. There is no reason to suspect that the mechanism of the reaction is different in one case from what is it in the other.

When we come to the phenols, the behavior of the two bodies is the same, even to the formation of the colored compounds. This further complicates the reasoning, as we have not only, as in the case of the anilides, an unsymmetrical body giving a symmetrical compound in part, but also, in the case of the phenols, a symmetrical compound giving a presumably unsymmetrical body, and that too in practically the same proportions in which it is formed from the unsymmetrical chloride.

The fact as shown by List and Stein[35] that the reduction of the symmetrical acid chloride gives the sulphobenzid, (I) has its most direct and reasonable explanation in the formation from (II), which is, however, the formula given for the unsymmetrical chloride.

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[35] Ber., 31, 1648, 1898.

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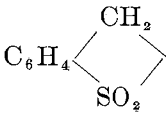
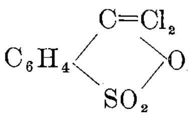


II



This tends to cast a doubt on the situation, as it negatives partly, at least, by its influence the positive results given by the ammonia derivatives in favor of the other view.

Tautomeric change is not a suitable explanation, where the two bodies are so distinctly differentiated from one another, unless the mechanism of the reactions shows definitely how such change does occur. No proof for any such mechanism has been produced. The discovery of the two crystalline forms of the symmetrical acid chloride may or may not have a bearing on the question.

From a physical standpoint, the work on our acid confirms by analogy the work done by Remsen and his students upon this class of bodies.

SUMMARY.

1. Two acid chlorides, the symmetrical with a melting point of 134°, the unsymmetrical with a melting point of 83°, have been prepared. These bodies were peculiar only in that they could be separated by fractional crystallization from solution, and that when pure, they did not tend in the least to form constant melting mixtures. Two crystalline forms of the symmetrical acid chloride were isolated, but their differences were not investigated closely.
2. The derivative obtained by the action of ammonia upon the symmetrical acid chloride was the ammonium salt of the imide. From this the imide itself was prepared by the action of dilute hydrochloric acid. The silver salt and the potassium salt of the imide also were made and analyzed.
3. The derivative obtained by the action of ammonia on the unsymmetrical acid chloride was the ammonium salt of the cyan acid; no imide was found. The silver and potassium salts of the cyan acid also were made and analyzed.
4. The derivatives obtained by the action of aniline on the symmetrical acid chloride were the symmetrical dianilide and the anil.
5. The derivatives obtained by the action of aniline on the unsymmetrical acid chloride were the symmetrical dianilide and the unsymmetrical dianilide.

6. By the action of phosphorous oxychloride, each of the two dianilides was transformed into the dianil. This in turn when heated with concentrated hydrochloric acid gave the anil or, heated with glacial acetic acid it gave the unsymmetrical dianilide.

7. The derivative obtained by the action of the alcohols on the symmetrical acid chloride was the benzoic ester of the sulphonic acid.

8. The derivatives obtained by the action of alcohols on the unsymmetrical acid chloride were the benzoic ester of the sulphone chloride, and the benzoic ester of the sulphonic acid.

9. The derivative obtained by the action of phenol upon either of the acid chlorides was always the diphenyl ester. No particular effort was made to prepare the phenyl sulphone chloride. When pyridine was used in the reaction, a second body was formed which may be the pyridine salt of the phenyl benzoic ester acid. Its constitution was not established.

10. By the action of methyl iodide on the silver salt of the methyl benzoic ester acid, the dimethyl ester was formed.

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