This class of compounds will be further studied, in connection with the action of haloid acids as catalytic agents.

Various other reactions were tested with derivatives of ammonia and it was found that the intensity of reaction varied directly with the positive character of the substituted radicle in the ammonia molecule. Ammonia gas and urethane both form crystalline addition products but the addition product of aniline was the only one which has yet been thoroughly studied.

Action of Aniline on Methyl Oxomalonate.—A molecular quantity of aniline dissolved in an equal volume of sodium-dry ether was added drop by drop to one molecule of keto ester. The reaction was intense, with considerable heat liberated. After the substance stood in a freezing mixture for a few minutes it began to crystallize in little balls of needles. It formed a solid, yellow tinted mass. It was then filtered and washed carefully with dry ether. After crystallizing from the same solvent it was filtered on a pump, washed, and then dried in a vacuum desiccator over sulphuric acid. The yield was quantitative.

Calculated for $(C_6H_5NH)(HO)C(CO_2CH_3)_2$: C, 55.23; H, 5.44; N, 5.85
Found: C, 55.25; H, 5.54; N, 6.22

Methyl anilinotartronate melts at 102° and is a pure white, crystalline substance. It is easily soluble in hot methyl alcohol, acetone, and hot ethyl alcohol, is fairly soluble in cold ethyl and methyl alcohols and benzene, slightly soluble in carbon tetrachloride, ligroin and carbon bisulphide, and very slightly soluble in water. Hydrochloric acid forms a colorless solution. Nitric acid forms a deep colored liquid, which when diluted with water turns a light green after discharging the blue color. Hot water dissociates it and gives methyl dihydroxymalonate and when the product cools aniline separates out as an emulsion of characteristic appearance and odor.

Several very interesting reactions have been studied with methyl anilinotartronate, the most important being the action of phosphorus pentoxide upon it, forming methyl phenyliminomalonate, $C_6H_5N = C(CO_2CH_3)_2$. This substance appears to be an analogue of phenyl isocyanate, and is extremely reactive at the point of double union of the carbon and nitrogen atoms. These reactions are being studied further. The senior author and his coworkers have been engaged for some time in a comprehensive study of oxomalonic esters with various acid amides, primary and secondary amines, and other classes of compounds having easily dissociated hydrogen atoms. The further results of these investigations will appear soon in THIS JOURNAL.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA.]

6-NITRO-3-METHYL-4-SULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

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In a previous paper by Karslake and Bond[1] upon an investigation of the oxidation products of 6-nitro-1-3-dimethylbenzene-4-sulphonic acid, a dilute alkaline solution of potassium permanganate being used as the oxidant, it was shown that three different acids were obtained which were regarded as 4-nitro-5-methyl-2-sulphobenzoic acid (I), 6-nitro-3-methyl-4-sulphobenzoic acid (II), and 6-nitro-4-sulphoisophthalic acid

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[1] THIS JOURNAL, **31**, 405.

(III) respectively. The constitution of each was based partly upon the fact that the first (I) was a dibasic acid which yielded *two* acid-chlorides, the second (II) a dibasic acid which gave only *one* acid-chloride, and the third (III) a tribasic acid which, like the first, gave *two* acid-chlorides.

Of the 6-nitro-3-methyl-4-sulphobenzoic acid and its derivatives, only the acid potassium salt was analyzed; the acid-chloride and acid-amide were prepared, but only their melting-points determined. In order to more definitely characterize the acid, since it does not appear to have ever been described in the literature, it was thought worth while to prepare, analyze and study the free acid and some of its more important derivatives. For this purpose, the acid potassium salt was prepared and used as initial material. A portion of the salt was converted into the acid-chloride, and from the acid-chloride the free acid, the amide, several anilides and the dimethyl ester were prepared. The neutral silver and lead salts were prepared by treating the acid potassium salt with silver nitrate and lead nitrate respectively, while the other salts were prepared, in general, by the action of their soluble chlorides upon the neutral silver salt.

Experimental.

6-Nitro-3-methyl-4-sulphobenzoic Acid: Acid Potassium Salt, $(NO_2)(CH_3)C_6H_2(SO_2OK)(COOH) + H_2O$. — This salt has already been described by Karslake and Bond and separates in well-defined plates which lose their water of crystallization when heated to 150°. It is much less soluble in cold than in hot water, quite insoluble in cold hydrochloric acid, insoluble in organic solvents. Found: H_2O, 5.83, 5.85; K, 12.30, 12.32. Calculated: H_2O, 5.68; K, 12.33.

Neutral Potassium Salt, $C_8H_5NSO_7K_2 + H_2O$.—This salt may be obtained directly from the solution upon the oxidation of 6-nitro-1,3-dimethylbenzene-4-sulphonic acid with potassium permanganate. It may be also prepared by neutralizing the acid potassium salt with caustic potash or potassium carbonate. It separates in prismatic plates of a yellow color which lose their water of crystallization below 210°. It is much more soluble in water than the acid potassium salt. Found: H_2O, 4.69; K, 21.79. Calculated: H_2O, 5.07; K, 22.04.

Acid Chloride, $(NO_2)(CH_3)C_6H_2(SO_2Cl)(COCl)$.—20 grams of the acid potassium salt were mixed with 30 grams of phosphorus pentachloride and warmed upon the water-bath for an hour. The sirupy mass thus obtained was poured into ice water and thoroughly washed. It soon solidified, was filtered off, dried between filter paper, and crystallized from a mixture of carbon tetrachloride and chloroform. It separates in prismatic plates, m. p. 90.2° (corr.). Yield, 13 grams. It is readily soluble in chloroform or ether, less so in carbon tetrachloride or benzene, insoluble in water. Found: Cl, 23.72, 23.75; S, 10.59, 10.70. Calculated: Cl, 23.8; S, 10.77.

Free Acid, $(NO_2)(CH_3)C_6H_2(SO_2OH)(COOH) + H_2O$.—4 grams of the acid-chloride were boiled with water until dissolved, which required about four hours. Upon evaporating to a thick sirupy solution, and allowing to stand for several days in a covered beaker, long, colorless, flat needles crystallized out which contained one molecule of water of crystallization. The hydrated acid melts at 34–37°, but upon heating to 110° it loses its water of crystallization and then melts at 150.7° (corr.).

It is very soluble in water and most organic solvents. Sulphur was determined by the sodium peroxide method,[1] nitrogen by the Kjeldahl method. Found: H_2O, 6.44, 6.39; S, 11.67, 11.65; N, 5.25, 5.08; H (acid), 0.73, 0.74. Calculated: H_2O, 6.45; S, 11.74; N, 5.02; H (acid), 0.72.

Acid Amide, $(NO_2)(CH_3)C_6H_2(SO_2NH_2)(CONH_2)$.—4 grams of the acid chloride were dissolved in chloroform and the solution saturated with dry ammonia. A light colored precipitate was formed. The chloroform was evaporated off, the residue washed with water, and crystallized from 50 per cent. alcohol. Small prismatic plates were obtained, m. p. 273–274°. Yield, 2 grams. It is soluble in ether, alcohol, chloroform, slightly soluble in hot water. Found: S, 12.26, 12.08; N, 15.49, 16.02. Calculated: S, 12.35; N, 16.29.

Dianilide, $(NO_2)(CH_3)C_6H_2(SO_2.NHC_6H_5)(CO.NHC_6H_5)$.—4 grams of the acid-chloride in chloroform solution were treated with a slight excess of aniline. A rather vigorous reaction set in, heat was evolved, and a light colored precipitate separated. The mixture was evaporated to dryness on the water bath, the residue treated with an aqueous caustic potash solution, separated from the excess of aniline, and acidified with dilute hydrochloric acid. The precipitate formed was filtered off and crystallized from 70 per cent. alcohol. Small, yellow, rectangular(?) plates were obtained, m. p. 244.8° (corr.). Soluble in organic solvents and aqueous solutions of fixed alkalies, insoluble in water and acids. Sulphur was determined by Pringsheim's method, nitrogen by the Kjeldahl method. Found: S, 7.55, 7.49; N, 10.43, 10.38. Calculated: S, 7.79; N, 10.24.

Di-o-toluidide.—3 grams of the acid chloride in chloroform solution were treated with a slight excess of *o*-toluidine. Heat was evolved, the solution turned red in color, and a precipitate separated out. The chloroform was evaporated off, the residue washed with dilute hydrochloric acid, dissolved in dilute caustic soda solution, filtered, and reprecipitated with dilute acid. The precipitate upon crystallization from a 70 per cent. alcohol gave fine, greenish yellow prisms, m. p. 238.7° (corr.). Yield, 1.2 grams. Soluble in most organic solvents, and in alkaline solutions, insoluble in water and dilute acids. Found: N, 9.59, 9.64; S, 7.38, 7.46. Calculated: N, 9.58; S, 7.46.

Di-m-toluidide and *di-p-toluidide* were prepared in a similar manner. The first separates from dilute alcohol in small, flat, bright yellow needles or prisms, m. p. 208.8° (corr.). Found: N, 9.81, 9.73; S, 7.38, 7.32. Calculated: N, 9.58; S, 7.46. The second separates from dilute alcohol in slender, colorless needles, m. p. 241.8° (corr.). Found:. N, 9.61, 9.63; S, 7.40, 7.35. Their solubilities are similar to the *o*-toluidide.

Dimethyl Ester, $(NO_2)(CH_3)C_6H_2(SO_2OCH_3)(COOCH_3)$.—To a solution of sodium methylate, made by dissolving 1 gram sodium in excess of anhydrous methyl alcohol, was added 0.6 gram acid chloride. The solution at first turned to a bright green color but after boiling for about an hour with a return condenser upon a water bath it changed to a pink. The sodium chloride which separated out was filtered off and the filtrate evaporated to small bulk. The dimethyl ester separated in small filaments forming a rather compact mass. After two crystallizations, and treatment with animal charcoal, it was obtained perfectly white. It is very soluble in water, fairly so in methyl alcohol, ethyl alcohol, chloroform, carbon tetrachloride, benzene, ligroin. It chars without melting at 302–305°. Found: N, 4.92, 4.95; S, 11.16, 11.02. Calculated: N, 4.85; S, 11.09.

Neutral Silver Salt, $C_8H_5NSO_7Ag_2$.—30 grams of the acid potassium salt were dissolved in hot water and treated with a concentrated solution of 36 grams silver nitrate. From the filtered solution, after evaporation to a relatively small volume,

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[1] Pringsheim, *Ber.*, **36**, 4244; **38**, 2459.

there separated, upon cooling, a good quantity of fine, colorless needles which contain no water of crystallization. Yield, 26 grams. Found: Ag, 45.23, 45.29. Calculated: Ag, 45.55.

Neutral Sodium Salt, $C_8H_5NSO_7Na_2 + 3H_2O$.—4 grams (1 mole) of the silver salt were dissolved in warm water and to it was added a solution of 1 gram (1 mole) of sodium chloride. Upon filtering off the precipitated silver chloride, evaporating the filtrate to a small volume and allowing to cool, there separated small, thin, elongated, almost colorless plates. They lose their water of crystallization below 210°. Found: H_2O, 15.15, 15.02; Na, 12.77, 12.68. Calculated: H_2O, 15.03; Na, 12.83.

Acid Sodium Salt, $C_8H_6NSO_7Na + 4H_2O$, obtained by treating the neutral sodium salt with hydrochloric acid, separates in prisms. Found: H_2O, 20.21, 20.10; Na, 6.45, 6.49. Calculated: H_2O, 20.17; Na, 6.45.

Neutral Calcium Salt, $C_8H_5NSO_7Ca + 2H_2O$, crystallizes in light yellow prisms. Found: H_2O (at 210°), 10.80, 10.78; Ca, 11.84, 11.80. Calculated: H_2O, 10.80; Ca, 11.93.

Acid Calcium Salt, $(C_8H_5NSO_7)_2Ca + H_2O$, made by the neutral salt with hydrochloric acid, separates in two crystalline forms, from warm concentrated solutions in small, colorless plates, from cold dilute solutions in large, yellow, square plates. Found: (first form) H_2O, 5.91; Ca, 6.63; (second form) H_2O, 6.11, Ca, 6.72. Calculated: H_2O, 6.03; Ca, 6.68.

Neutral Barium Salt, $C_8H_5NSO_7Ba + 2H_2O$.—This salt is best obtained by adding a solution of barium chloride to a rather concentrated solution of the neutral potassium salt. It seems to separate best from the hot solution as it slowly evaporates upon the water bath. It crystallizes in transparent crystals (prisms) arranged in groups of a slight yellow color. Found: H_2O, 8.02; Ba, 32.28. Calculated: H_2O, 8.33; Ba, 31.77.

Acid Barium Salt, $(C_8H_6NSO_7)_2Ba + 4H_2O$, is prepared by adding a solution of barium chloride to a hot solution of the acid potassium salt. Upon cooling, the salt crystallizes out in beautiful white needles. Found: H_2O, 10.00, 9.90; Ba, 18.70, 18.69. Calculated: H_2O, 9.87; Ba, 18.84.

Neutral Strontium Salt, $C_8H_5NSO_7Sr + 2H_2O$, separates in small, colorless needles. Found: H_2O, 9.46, 9.37; Sr, 22.87, 22.65. Calculated: H_2O, 9.38; Sr, 22.82.

Acid Strontium Salt, $(C_8H_6NSO_7)_2Sr + H_2O$, separates from warm concentrated solutions in long, narrow, colorless plates, and from cold dilute solutions in splendid yellow octahedrons (?). Found: (plates) H_2O, 5.63; Sr, 15.10; (octahedrons ?) H_2O, 5.72; Sr, 14.85. Calculated: H_2O, 5.63; Sr, 14.93.

Neutral Ammonium Salt, $C_8H_5NSO_7(NH_4)_2$, crystallizes in fine colorless needles. It is anhydrous. Found: N (ammoniacal), 11.94, 12.06. Calculated: 11.91.

Neutral Magnesium Salt, $C_8H_5NSO_7Mg + 4H_2O$, separates in small colorless prisms, very soluble in water. Found: H_2O, 20.29, 20.18; Mg, 6.84, 6.79. Calculated: H_2O, 20.27; Mg, 6.85.

Neutral Zinc Salt, $C_8H_5NSO_7Zn + 3H_2h$, short needles, very soluble in water. Found: H_2O, 14.23, 14.35; Zn, 17.16, 17.28. Calculated: H_2O, 14.27; Zn, 17.27.

Neutral Copper Salt, $C_8H_5NSO_7Cu$, crystallizes in anhydrous, light blue needles, quite soluble in water. The copper was determined by electrolysis after conversion to copper sulphate. Found: Cu, 19.4, 19.53. Calculated: Cu, 19.71.

Neutral Lead Salt, $C_8H_5NSO_7Pb + 2H_2O$, made by treating the acid potassium salt with excess of a solution of lead nitrate, separates in small, colorless rectangular (?) plates. Found: H_2O, 2.11, 2.09; Pb, 43.84, 43.72. Calculated: H_2O, 1.94; Pb, 43.55.

IOWA CITY, IA.