of no particular importance; we have found it convenient to take an amount approximately equal to that of the material under examination.

The method has been tested by the junior author, who received a number of mixtures, the composition of each of which was unknown to him. His results were accurate to 2 per cent. and in some cases agreed even more closely.

In dealing with ternary mixtures it is advisable to crystallize them fractionally from alcohol once or twice. In this manner we have found that we could obtain two portions, one containing substantially all the orthonitraniline together with some meta-, while the other portion consisted of the meta- and paraisomers. We have made a few experiments on the separation of ortho- and paranitraniline by crystallization. So far as we can judge, the separation can be made quantitatively. The mixture is weighed and treated with just sufficient boiling alcohol (95 per cent.) to dissolve it. When cool, the volume is measured. The paranitraniline which deposits is collected and to its weight is added that of the quantity dissolved in the filtrate; the sum of these, subtracted from the weight of the original material, represents the orthonitraniline.

Summary,

1. Curves have been constructed showing the relationship between the melting points and the composition of the three binary mixtures of the isomeric nitranilines.

2. In the case of the mixtures of ortho- and meta- and of meta- and paranitraniline, these curves are comparatively regular; they fall to the eutectic point and then rise to the melting point of the pure compound.

3. The curve representing the relationship between the melting point and composition of mixtures of ortho- and paranitraniline is highly irregular. At present it is impossible to give a satisfactory explanation of this phenomenon.

4. The curves mentioned above can be used to determine the composition of mixtures of otho- and meta- and of meta- and paranitraniline, respectively, by a simple and expeditious method which requires only a minimal quantity of material. The results are usually accurate within two per cent.

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SOME DERIVATIVES OF 1,3-DIMETHYL-2,6-DINITROBENZENE-4-SULPHONIC ACID,

By W. J. Karslake and W. J. Morgan.

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The initial material used was the potassium salt of 1,3-dimethyl-2,6-dinitrobenzene-4-sulphonic acid, which was prepared as follows:[1] 800

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[1] Claus and Schmidt, *B.* 19, 1424.

cc. commercial *m*-xylene were shaken in a separatory funnel with 800 cc. sulphuric acid, sp. gr. 1.84, for about an hour, no attempt being made to regulate the rise in temperature. After standing for an hour or so the *m*-xylenesulphonic acid solution was drawn off from the undissolved portion of the hydrocarbons and slowly added, with constant shaking, to a mixture of 1000 cc. of ordinary fuming nitric acid and 500 cc. of ordinary fuming sulphuric acid, the temperature being kept below 100°. After standing twenty-four hours, the mixture was heated to 125–130° for six or seven hours, allowed to cool, and poured into about eight liters of cold water. After filtering off the insoluble precipitate formed, which consists mostly of 2,4,6-trinitro-*m*-xylene, the filtrate was heated, neutralized with calcium carbonate, again filtered, and a hot solution of potassium carbonate added in excess. The precipitated calcium carbonate was filtered off, the filtrate evaporated to a volume of three or four liters and the potassium salt of 1,3-dimethyl-2,6-dinitrobenzene-4-sulphonic acid allowed to crystallize out. A yield of 640 grams was obtained and from the melting-point of the sulphonchloride, and sulphonamide, its identity established. It was later learned that a better yield and a purer product could be obtained by isolating the 1,3-dimethyl-6-nitrobenzene-4-sulphonic acid first formed and then nitrating this with about twice its weight of fuming nitric acid diluted with double the weight of ordinary sulphuric acid, sp. gr. 1.84.

The sulphonchloride was made in the usual manner by treating the potassium salt with an excess of phosphorus pentachloride, pouring the product into ice-water, filtering and washing, and crystallizing the residue from carbon tetrachloride. It had a melting-point of 123°.

1,3-Dimethyl-2,6-dinitrobenzene-4-sulphonanilide.—Twenty grams of aniline dissolved in 100 cc. carbon tetrachloride were added to 20 grams of the sulphonchloride previously dissolved in 200 cc. carbon tetrachloride. After heating on the water-bath for two hours in a flask connected with a return condenser the carbon tetrachloride was distilled off, the residue washed several times with dilute hydrochloric acid and afterwards with water. It was then dissolved in a ten per cent. solution of caustic potash, filtered, the filtrate acidified, with dilute hydrochloric acid, and the precipitated anilide crystallized from dilute alcohol. It separated in short, yellow needles which melted at 154°. It is easily soluble in ether or chloroform, less so in carbon tetrachloride, and insoluble in water. Upon analysis it gave 9.02 per cent. sulphur (Liebig's method) against 9.12 per cent. calculated for $C_{14}H_{13}O_6N_3S$.

1,3-Dimethyl-2,6-dinitrobenzene-4-sulphon-o-toluidide. — Five grams of the sulphonchloride dissolved in 30 cc. of carbon tetrachloride were added to four times the equivalent weight of *o*-toluidine previously dissolved in 100 cc. of carbon tetrachloride and the mixture heated in a flask with a return condenser for four hours on the water bath. After distilling off the carbon tetrachloride the residue was treated as in the preparation of the anilide. From ninety-five per cent. alcohol the *o*-toluidide separated in white radiating nodules, while from a mixture of benzene and alcohol it crystallized in white needles. It had a melting-point of 135°. Upon analysis it gave 8.68 per cent. sulphur against 8.76 per cent. required for $C_{15}H_{15}O_6N_3S$.

1,3-Dimethyl-2,6-dinitrobenzene-4-sulphon-p-toluidide.—Three times the equivalent weight of *p*-toluidine was heated with 5 grams of the sulphonchloride in the presence of dilute caustic potash for about half an hour on the water-bath. The mixture was then filtered and the filtrate acidified with dilute hydrochloric acid until no further precipitation took place. The *p*-toluidide so obtained was crystallized from alcohol and separated in yellow plates or in silky needles having a melting-point of 162°. It is soluble in chloroform, less so in carbon tetrachloride, and insoluble in water. Upon analysis it gave 8.96 per cent. sulphur against 8.76 required by theory.

1,3-Dimethyl-2,6-dinitrobenzene-sulphone-benzene.—Five grams of the sulphonchloride were dissolved in an excess of benzene and one gram of anhydrous aluminum chloride added. The mixture was then heated for three hours in a flask with a reflux condenser on the water-bath. The excess of benzene was distilled off and the residue successively treated with dilute caustic soda solution, dilute hydrochloric acid and water, and then dried. It was finally digested with carbon tetrachloride and a small quantity of boneblack, filtered, and allowed to cool. The sulphone separated in large glistening plates, which melted at 178°. Upon analysis it gave 9.70 per cent. sulphur against 9.52 per cent. required for $C_{14}H_{12}O_6N_2S$.

1-Carboxy-3-methyl-2,6-dinitrobenzene-4-sulphonic Acid(?).—Eight hundred grams of the potassium salt of 1,3-dimethyl-2,6-dinitrobenzene-4-sulphonic acid were dissolved at room temperature in five liters of water and to it was added a solution of 1700 grams of potassium permanganate, 50 grams of caustic potash, and enough water to dilute the whole to 120 liters. After standing three weeks at room temperature the solution was warmed on the water-bath, decolorized by the addition of a little alcohol, filtered from the manganese dioxide, and evaporated to crystallization. One hundred grams of unchanged original potassium salt separated out. This was filtered off, the filtrate acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol. The alcoholic solution upon evaporation to dryness gave a sirupy liquid which was treated with phosphorus pentachloride, poured into ice-water, the insoluble residue thoroughly washed with water and, after drying, crystallized from carbon tetrachloride. The crystals thus obtained were brown in color, granular, and irregular in shape. They melted at 127–128° and were probably an impure acid chloride. Upon digestion with concentrated aqueous ammonia they formed a product which, upon crystallization from alcohol, gave yellow plates possessing no definite melting-point and charring at about 290°. They were not analyzed. The residue, which was insoluble in alcohol, was recrystallized several times from water and then analyzed. The results obtained indicate that one of the two methyl groups, CH_3, present in the original salt, was oxidized to the corresponding carboxyl group, CO.OH, but it yet remains to be shown which one of them it was. We are hoping to determine this point in the near future. Tentatively it is assumed to be that methyl group which is in the first position (1). Upon this assumption the salt obtained was the acid potassium salt of 1-carboxy-3-methyl-2,6-dinitrobenzene-4-sulphonic acid and contains one molecule of water of crystallization. The analysis gave 11.04 per cent. potassium, 5.00 per cent. water, 9.00 per cent. sulphur, against 11.08 per cent. potassium, 4.97 per cent. water, 8.83 per cent. sulphur required by theory.

The *acid barium salt* was obtained by adding barium carbonate to the hot solution of the acid potassium salt, filtering, and adding hydrochloric acid to the filtrate. Upon coooling there separated yellow plates containing three molecules of water of crystallization. The analysis gave 15.59 per cent. barium, 12.68 per cent. water, compared to 16.06 per cent. barium, 12.62 per cent. water calculated according to theory.

The *neutral barium salt* was prepared by adding barium carbonate to the hot solution of the acid potassium salt and filtering. It separated in light yellow plates containing no water of crystallization. The analysis gave 30.98 per cent. barium against 30.90 per cent. barium required by theory.

The *neutral strontium salt* was formed by adding strontium carbonate to the hot solution of the acid potassium salt and filtering. It separated in almost white, square crystals containing no water of crystallization. The analysis gave 21.81 per cent. strontium against 22.08 per cent. required by theory.

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CONCERNING α-DINAPHTHYL SELENIDE AND TELLURIDE.

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Some years ago, while collecting and tabulating material for the comparative study of the periodic relationship in the oxygen family, especially in the organic combinations of sulphur, selenium and tellurium, we were led to undertake the synthesis of certain aromatic compounds of