

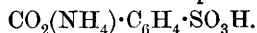
XXXIX.—*o*-Cyanobenzenesulphonic Acid and its
Derivatives.

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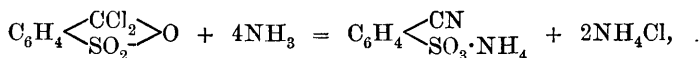
o-CYANOBENZENESULPHONIC ACID is first mentioned by Jesurun (*Ber.*, 1893, **26**, 2288), who states that it is formed when *o*-cyanobenzene-sulphonic chloride, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$, is boiled with water. He did not,

however, isolate the acid, but described its sodium salt. When heated under pressure at 95–100° with a small quantity of water for a long time, the chloride yields *o*-benzoic sulphonamide, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$, this being converted at 180° into ammonium *o*-benzoic sulphonate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\cdot\text{NH}_4$.

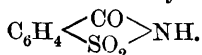
Remsen (*Amer. Chem. J.*, 1895, 17, 309) and Remsen and Saunders (*ibid.*, 347) describe the formation of ammonium *o*-cyanobenzenesulphonate by the action of aqueous ammonia on the unsymmetrical dichloride of *o*-sulphobenzoic acid, and Remsen and McKee (*ibid.*, 1896, 18, 794) also obtained this ammonium salt from the corresponding symmetrical chloride, whilst Remsen and Karslake (*ibid.*, 819) prepared it from a mixture of the symmetrical and unsymmetrical chlorides, and obtained the sodium, potassium, and barium salts by treating the ammonium salts with the corresponding hydroxides. They could not isolate the free acid, the barium salt yielding with dilute sulphuric acid *o*-benzaminosulphonic acid, $\text{CO}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, and the ammonium salt with dilute hydrochloric acid, ammonium *o*-benzaminosulphonate, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\cdot\text{NH}_4$. On heating ammonium *o*-cyanobenzenesulphonate with hydrochloric acid in a sealed tube, they obtained acid ammonium *o*-sulphobenzoate,



List and Stein (*Ber.*, 1898, 31, 1648) showed that the two dichlorides of *o*-sulphobenzoic acid are tautomeric, and called Remsen's symmetrical and unsymmetrical forms "stable" and "labile" respectively. They found that ammonia rapidly converts the labile chloride in ethereal solution into Remsen and Saunders' ammonium *o*-cyanobenzenesulphonate,



but acts slowly on the stable chloride to form *o*-benzoic sulphinide,



Jesurun prepared *o*-cyanobenzenesulphonic chloride (*loc. cit.*) by heating "saccharin" (1 mol.) with phosphorus pentachloride (2 mols.) in a sealed tube for two hours at 70–75°. We have found it better to heat the mixture under the atmospheric pressure for about two hours at 130°. Ether is a more suitable solvent than benzene, a fact noted independently by List and Stein (*loc. cit.*), who obtained the chloride by treating ammonium *o*-cyanobenzenesulphonate with phosphorus pentachloride.

By concentration of the aqueous mother liquor obtained in the preparation of *o*-cyanobenzenesulphonic chloride by a modification of Jesurun's method, we have isolated *o*-cyanobenzenesulphonic acid,

$\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$; it crystallises from water in white needles melting at $279-279.5^\circ$. The silver salt was prepared by dissolving the acid in an aqueous solution of the calculated quantity of sodium carbonate and adding the requisite amount of silver nitrate dissolved in water. When heated on the water-bath with fuming nitric acid, *o*-cyanobenzenesulphonic acid yields two substances, white needles melting at $255-255.5^\circ$ and a smaller quantity of yellow, prismatic crystals melting between 140° and 150° . The action of bromine on the acid has been investigated, and it has also been shown that it is not reduced by zinc dust and boiling water.

On reduction of *o*-cyanobenzenesulphonic chloride with zinc dust, there is formed zinc *o*-cyanobenzenesulphinat, $(\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2)_2\text{Zn}$. Heating the crude reaction product with a solution of sodium carbonate converts this salt into the corresponding sodium *o*-cyanobenzenesulphinat, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Na}$, which forms a green solution. This sodium salt was not isolated. When its solution is acidified with dilute sulphuric acid, *o*-cyanobenzenesulphinic acid, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{H}$, is precipitated; it crystallises from glacial acetic acid in small, white needles melting at $226.5-228^\circ$. When heated on the water-bath with 2*N*-sodium hydroxide, *o*-cyanobenzenesulphonic chloride yields a solution from which hydrochloric acid does not precipitate the sulphonic acid, but a substance, probably *o*-benzoic sulphinide, melting at $221.5-223^\circ$ and possessing the sweet taste of "saccharin." With bromine, *o*-cyanobenzenesulphinic acid yields two compounds melting at $156-156.5^\circ$ and $172.5-173^\circ$ respectively. Neither of these substances contains bromine. When treated with nitrous acid by König's method (*Ber.*, 1878, 11, 615), *o*-cyanobenzenesulphinic acid is converted into a yellow solid, probably *o*-cyanodibenzsulphohydroxamic acid, $(\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2)_2\text{NOH}$.

The further reduction products of *o*-cyanobenzenesulphonic acid and *o*-cyanobenzenesulphinic acid by chemical and electrolytic methods are now under investigation. A future communication will treat of the results of these experiments, of the substances obtained by the action of nitric acid on *o*-cyanobenzenesulphinic acid, and of bromine and nitrous acid on *o*-cyanobenzenesulphinic acid, and of amino-derivatives resulting from the interaction of *o*-cyanobenzenesulphonic chloride and various amino-compounds.

EXPERIMENTAL.

o-Cyanobenzenesulphonic Chloride, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$.

Jesurun (*Ber.*, 1893, 26, 2228) prepared this substance by heating "saccharin" (1 mol.) with phosphorus pentachloride (2 mols.) in a sealed tube for two hours at 75° . The product was poured on to ice,

the chloride separating as an oil, which solidified, and, after drying in the air, was crystallised from benzene and obtained in prismatic crystals melting at 69—70°. The following procedure gives more satisfactory results.

Thirty grams of commercial "insoluble saccharin" (or "soluble saccharin") and 70 grams of phosphorus pentachloride were heated in an Erlenmeyer flask with an air condenser for an hour and a half in a paraffin bath at 120—140°, much hydrochloric acid being evolved. The hot mixture was poured on to ice, and, after solidification of the oil, the crude chloride was collected and pressed on a porous plate, the yield being 32 grams. This was extracted twice with ether dried over sodium and the chloride obtained by concentrating the solution. The residue after extraction consisted of 5 grams of unchanged "saccharin," and was worked up again for the chloride. After trituration with a 1 per cent. solution of sodium hydrogen carbonate to remove "saccharin," and repeated crystallisation from dry ether, the *o*-cyanobenzenesulphonic chloride was obtained in prismatic crystals melting constantly at 67.5°. Light petroleum was a less satisfactory solvent, but yielded small needles melting at 67—68°.

Jesurun (*loc. cit.*) gives the melting point of the crystals from benzene as 69—70°. List and Stein (*Ber.*, 1898, 31, 1648) used ether as a solvent and mention the same melting point. The chloride is readily soluble in cold ether, chloroform, acetone, benzene, and xylene, and in hot light petroleum and carbon disulphide; it has a slightly sweetish taste, but much less pronounced than that of "saccharin," and also has an acid flavour distinguishing it from this substance.

Action of Nitric Acid.—The chloride is dissolved by heating with fuming nitric acid on the water-bath, but not changed chemically.

Action of Sodium Hydroxide.—To 15 grams of the chloride, 65 c.c. of 2*N*-sodium hydroxide were added gradually, heat being evolved during the reaction. After the mixture had been heated for an hour and a half on the water-bath, solution was complete. While still hot, the liquid was acidified with 2*N*-hydrochloric acid, crystallisation being facilitated by stirring with a glass rod. The precipitate was collected and dried in the steam-oven. Five grams of product were obtained which melted without decomposition to a yellow liquid at 221.5—223°, proving that it was not *o*-cyanobenzenesulphonic acid, which melts at 279—279.5°. It had the sweet taste of "saccharin," and was probably *o*-benzoic sulphinide, although the analyses differ slightly from those required by $C_7H_5O_3NS$. The molecular weight obtained by the cryoscopic method with glacial acetic acid as solvent was 197, $C_7H_5O_3NS$ requiring 183.

o-Cyanobenzenesulphonic Acid, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$.

On evaporation of the aqueous mother liquor from the preparation of *o*-cyanobenzenesulphonic chloride, a white precipitate was obtained, which melted at $228-250^\circ$ to a colourless liquid and was soluble in dilute solutions of sodium hydroxide and sodium carbonate. The crude product was dissolved in dilute caustic soda and the solution extracted twice with ether. After removal of the ethereal layer, the acid was precipitated from the alkaline aqueous solution by acidification with dilute sulphuric acid, filtered off at the pump, thoroughly washed with water, and dried by pressing on a porous plate. By repeated crystallisation from water, the acid was obtained in the form of white needles melting at $279-279.5^\circ$, soluble in a large quantity of boiling water and in alcohol, and slightly soluble in boiling ether and chloroform.

0.2575 gave 17.5 c.c. moist nitrogen at 26° and 769 mm. $\text{N} = 7.63$.

0.19305 „ 0.2442 BaSO_4 . $\text{S} = 17.34$.

$\text{C}_7\text{H}_5\text{O}_3\text{NS}$ requires $\text{N} = 7.65$; $\text{S} = 17.48$ per cent.

Silver Salt.—Silver *o*-cyanobenzenesulphonate, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Ag}$, was prepared by the following method: 0.5 gram of the acid was dissolved in an aqueous solution of 0.1448 gram of anhydrous sodium carbonate and two drops of a concentrated aqueous solution of 0.4644 gram of silver nitrate added. The slight precipitate was filtered off, and on addition of the rest of the silver nitrate solution the silver salt was precipitated as a white solid. This was collected, washed with alcohol and then with ether, pressed out on a dry plate, and dried in an air-oven at $120-130^\circ$. The light was excluded as far as possible, but nevertheless the salt became somewhat dark in colour.

0.2520 gave 0.0929 Ag. $\text{Ag} = 36.86$.

$\text{C}_7\text{H}_4\text{O}_3\text{NSAg}$ requires $\text{Ag} = 36.90$ per cent.

Action of Bromine and Nitric Acid.—When heated with bromine, *o*-cyanobenzenesulphonic acid yielded a brownish-tinted, crude product, very soluble in alcohol, somewhat soluble in glacial acetic acid, and almost insoluble in benzene and light petroleum. Heating on the water-bath with fuming nitric acid converted *o*-cyanobenzenesulphonic acid into a yellowish-white, very hygroscopic substance, the crude product melting at 255° to a dark brown liquid. On crystallisation from glacial acetic acid, white, prismatic needles melting at $255-255.5^\circ$ were obtained, accompanied by a small proportion of yellow, prismatic crystals melting at $140-150^\circ$ with evolution of gas. On raising the temperature, the liquid resolidified, and the dark product melted again at about 230° to a black, viscid liquid.

o-Cyanobenzenesulphinic acid, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{H}$, was prepared as follows from *o*-cyanobenzenesulphonic chloride, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$: 40 c.c. of water were heated to boiling in a 300 c.c. Erlenmeyer flask, 10 grams of zinc dust added, and then, without further heating, 15 grams of finely-powdered *o*-cyanobenzenesulphonic chloride in small portions. The mixture was stirred frequently with a glass rod. At each addition of the chloride, an energetic reaction with evolution of heat ensued, and when all the chloride had been added the contents of the flask were heated for ten minutes over a small flame, allowed to cool, and filtered at the pump. To decompose the zinc sulphinate, the residue on the filter was heated for ten minutes with a solution of 20 grams of anhydrous sodium carbonate in 200 c.c. of water, filtered, and the residue washed with water. The filtrate was evaporated to half its volume, cooled, and acidified with dilute sulphuric acid. *o*-Cyanobenzenesulphinic acid was precipitated as a white solid, which was filtered off, a further quantity of the sulphinic acid being obtained by concentrating the filtrate. The acid was dried on a porous plate, the yield of crude product being about one-third of the weight of the chloride used; it melted at $217\text{--}225^\circ$ to a dark liquid and was crystallised by dissolving in hot glacial acetic acid, adding hot water until the solution became cloudy, clarifying by the application of heat, and finally allowing the liquid to cool. From this solvent, the sulphinic acid separated in clusters of small, white needles, which, when purified by repeated crystallisation, became moist at 220° and melted to a yellow liquid at $226\cdot5\text{--}228^\circ$. The yield was somewhat better when a large quantity of the chloride was employed.

0.1767 gave 13 c.c. moist nitrogen at 17° and 756 mm. $\text{N} = 8\cdot49$.

0.1618 „ 0.22725 BaSO_4 . $\text{S} = 19\cdot29$.

$\text{C}_7\text{H}_5\text{O}_2\text{NS}$ requires $\text{N} = 8\cdot38$; $\text{S} = 19\cdot16$ per cent.

In the nitrogen estimation, it was found better not to mix the sulphinic acid with copper oxide in the boat.

o-Cyanobenzenesulphinic acid is very slightly soluble in water, absolute alcohol, ether, benzene, light petroleum, or chloroform; it dissolves readily in hot glacial acetic acid. The sodium salt was obtained by treating the acid with the equivalent weight of aqueous sodium carbonate. On concentrating to small bulk, it separated in minute, white needles, which were very soluble in water and became dull in a desiccator through loss of water of crystallisation.

In preparing the acid, the *o*-cyanobenzenesulphonic chloride must not be mixed with the zinc dust in a mortar, since a vigorous reaction soon ensues, leaving a charred mass from which no sulphinic acid can be extracted.

An attempt was made to prepare *o*-cyanobenzenesulphinic acid by

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reducing an aqueous solution of *o*-cyanobenzenesulphonic acid in an analogous manner, but the sulphonic acid underwent no change.

Action of Bromine.—2·6 grams of *o*-cyanobenzenesulphinic acid were treated at the ordinary temperature with a solution of 2·6 grams of bromine in chloroform. The red colour of the bromine solution was almost immediately discharged, and excess of the bromine solution was then added until the colour persisted for an hour. The yellow solid was then filtered off, the crude product melting partially at 165—167° and completely at 178°. Its weight was equal to that of the sulphinic acid taken. It was dissolved in dilute caustic soda and reprecipitated by addition of dilute hydrochloric acid. On crystallising several times from water, it was obtained in white crystals melting at 172·5—173°. These dissolved fairly readily in water and alcohol, and very easily in ether and glacial acetic acid: they were insoluble in chloroform, light petroleum, and benzene. The substance contained no bromine, and its aqueous solution was strongly acid to litmus. In estimating the percentage of nitrogen, it was necessary to mix the compound in the boat with fine copper oxide.

0·1933 gave 13·3 c.c. moist nitrogen at 15° and 758 mm. N = 8·04.
 0·2037 „ 13·8 „ „ „ 17° „ 760 „ N = 7·87.
 0·1585 „ 0·2001 BaSO₄. S = 17·33.

On modifying the conditions, a different product resulted, also containing no bromine: 0·8 gram of *o*-cyanobenzenesulphinic acid was treated with 0·8 gram of bromine dissolved in chloroform. The bromine solution was almost instantly decolorised, with absorption of considerable heat and evolution of hydrobromic acid. The chloroform was volatilised by heating on the water-bath: the residue weighed 1·12 grams; 0·5 gram of bromine in solution was then added and evaporated off, but there was no further increase in weight. The crude product was red in colour; it was dried on a porous plate, and after several crystallisations from alcohol white needles melting at 156—156·5°, soluble in water and alcohol, and insoluble in chloroform, were obtained. On addition of water, the red crude product turns darker red, then white, and finally dissolves.

0·16055 gave 11·2 c.c. moist nitrogen at 18° and 764 mm. N = 8·10.
 0·13735 „ 0·1929 BaSO₄. S = 19·28.

The correct interpretation of the analyses of the two compounds obtained by the action of bromine on the sulphinic acid is still a matter of doubt. The percentages of nitrogen and sulphur required by certain formulæ are appended.

- (a) $(\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)_2$ requires N = 7.69 ; S = 17.58 per cent.
 (b) $(\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2)_2$ „ N = 8.43 ; S = 19.28 „ „
 (c) $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ „ N = 7.65 ; S = 17.48 „ „
 (d) $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{H}$ „ N = 8.38 ; S = 19.16 „ „

Substances with formulæ (a) and (b) have not been prepared previously. (c) and (d) represent *o*-cyanobenzenesulphonic acid and *o*-cyanobenzenesulphinic acid respectively. The melting points and other properties of the substances melting at 156—156.5° and 172.5—173° exclude the possibility of the identity of either with the sulphonic or sulphinic acid described in this paper.

We are indebted to Mr. R. S. Bowman, B.Sc., for analysing and determining the molecular weight of the *o*-benzoic sulphinide obtained from *o*-cyanobenzenesulphonic chloride by the action of dilute caustic soda.

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