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THE PREPARATION OF 1-METHYL - 2 - HYDROXY -
3 - DIAZOBENZENE - 5 - SULPHONIC ACID

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K. H. KLAASSENS and C. J. SCHOOT

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THE PREPARATION OF 1-METHYL-2-HYDROXY-3-DIAZO-
BENZENE-5-SULPHONIC ACID.

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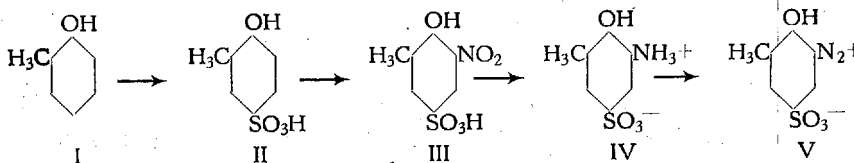
K. H. KLAASSENS and C. J. SCHOOT

(Philips Research Laboratories, N.V. Philips' Gloeilampenfabrieken,
Eindhoven - Netherlands).

The preparation of 1-methyl-2-hydroxy-3-diazobenzene-5-sulphonic acid, starting from o-cresol, is described. With a small quantity of a strong acid a suspension of 1-methyl-2-hydroxy-3-aminobenzene-5-sulphonic acid in a solution of sodium nitrite gives the sodium salt of the diazonium compound.

The preparation of 1-methyl-2-hydroxy-3-diazobenzene-5-sulphonic acid, as needed for photochemical work in this laboratory, can be divided into the preparation of the methyl-hydroxy-aminobenzene-sulphonic acid and the preparation of the diazonium compound.

Starting with o-cresol the amino compound was prepared by sulphonation, nitration and reduction.



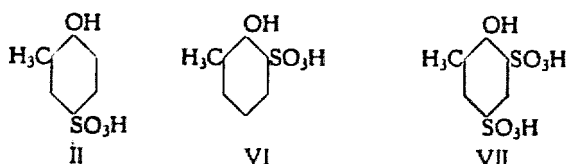
A method was followed whereby the products II and III were not separated and the compound IV was prepared in about twenty-four hours.

Little is known about the preparation of the compounds II, III and IV. *Claus* and *Jackson*¹⁾ obtained II by heating a mixture of o-cresol and concentrated sulphuric acid on a water bath for 8 to 10 hours. *Gomberg* and *Anderson*²⁾ heated the mixture for one hour. None of these authors give details about the yield.

¹⁾ A. Claus and U. A. Jackson, J. prakt. Chem. [2], 38, 330 (1888).

²⁾ M. Gomberg and L. C. Anderson, J. Am. Chem. Soc. 47, 2027 (1925).

There are three compounds which may be formed from the reaction of o-cresol with sulphuric acid, namely:



Having regard to the yield of IV, however, it is important to know, how much of II is formed. In the experimental section a method is described which proves that about 85 % of II is formed. It is found that when mixing o-cresol with concentrated sulphuric acid the temperature rises to 110 °C and the reaction is complete after about 15 minutes.

*Schultz*³⁾ prepared nitrocresol-sulphonic acid (III) by nitrating cresol-sulphonic acid (II), but he does not give any details. We have nitrated II with nitric acid as well as with potassium nitrate. In the latter case the monopotassium salt of III precipitates. This salt is very insoluble, reduction of the separated potassium salt of III giving the same yield as reduction of the potassium salt together with the mother liquid. Nitration with nitric acid gives somewhat higher yields.

The aminocresol-sulphonic acid (IV) was prepared by *Schultz*³⁾ by reducing the nitro compound with stannous chloride and hydrochloric acid. He reports that the compound crystallizes with half a molecule of water, but we found variable quantities of water. We have also investigated reduction with sodium sulphide, with cast iron and hydrochloric acid and electrolytic reduction. Reduction with sodium sulphide is carried out in an alkaline medium and after acidifying there is precipitation of some sulphur, which is difficult to remove, moreover the yield is somewhat smaller. Reduction with cast iron gives a smaller yield of a rather greyish product and the method is more laborious. Electrolytic reduction was investigated with a variation of voltage, density of current and cathode materials. The yield was in all cases less than when reducing with stannous chloride.

The diazonium compound (V) is very soluble in water (about 30 %). Diazotization with sodium nitrite and acid is therefore not suitable, since then the product is contaminated with the sodium salt of the acid used. We have diazotized IV with gaseous nitrous anhydride, the method which *Griess* used in 1858 for diazonium compounds rather insoluble towards V. The solubility of V requires

³⁾ G. Schultz, Ber. 40, 4319 (1907).

that the amount of water in which IV is suspended must be not too large⁴⁾. The diazonium compound crystallizes with amounts of water varying up to two molecules.

When suspending IV in a solution of sodium nitrite and adding a few drops of a strong acid, for instance concentrated fluoboric acid, a violent reaction takes place and after a few minutes all the amino compound is converted into the sodium salt of V. In the experimental section a more moderate method is described. The sodium salt crystallizes with 5 molecules of water.

Experimental Section.

Reaction of *o*-cresol and sulphuric acid.

10.9 g of *o*-cresol are mixed with 10 ml of concentrated sulphuric acid (sp.gr. 1.84). The temperature rises to 110—155°C. After 15 minutes the mixture is diluted with 300 ml of distilled water and the boiling solution is treated with an excess of barium carbonate. Assuming the barium salt of VI to be entirely insoluble and the barium salts of II and VII very good soluble, the precipitate consists of a mixture of barium sulphate, the barium salt of VI and the excess of barium carbonate; the filtrate contains only the barium salts of II and VII. The precipitate is filtered off and washed, distilled water then being added to the filtrate to make it up to 1000 ml. Analysis of 5 ml of the filtrate yielded 0.0660 and 0.0661 g of barium sulphate. It has been calculated that 87 % of II and 13 % of VII is formed, assuming that VI is not formed at all.

The precipitate, consisting of barium sulphate, the barium salt of VI and barium carbonate, is first washed with dilute hydrochloric acid to remove barium carbonate and afterwards washed with distilled water. After drying the weight of the precipitate was 14.7072 g. After heating with concentrated sulphuric acid a part of this mixture weighing 1.3733 g there was found to be a loss of weight of 0.0369 g. A calculation shows that less than 2 % of VI is formed. At least 85 % of the desired sulphonic acid (II) is therefore formed.

Preparation of 1-methyl-2-hydroxy-3-aminobenzene-5-sulphonic acid.

Five hundred grams of molten *o*-cresol (about 30° C) and 500 ml of concentrated sulphuric acid (sp. gr. 1.84) are mixed in a two-litre round-bottomed flask. The flask is warmed on a water bath for one hour and the liquid is stirred with a mechanical stirrer. The cooled mixture is poured into an enamelled vessel containing 2 litres of distilled water. The stirred solution is cooled to about 30° C and 330 ml of concentrated nitric acid (sp.gr. 1.37) are allowed to flow dropwise into the solution, during one and a half hours; the temperature should not rise above 40° C. Stirring is continued for another hour after the addition is complete, the mixture then being quickly heated to the boiling temperature. A mixture of 3300 ml stannous chloride solution containing 67 g SnCl₂ per 100 ml and 1—3 % hydrochloric acid, and two litres of concentrated hydrochloric acid (sp. gr. 1.19) is added during a period of 15 minutes, taking care that the contents of the flask do not foam over the rim. The solution is allowed to boil for another 5 minutes and thereafter slowly cooled during the night. The crystallized amino compound is collected on a Büchner

⁴⁾ R. J. H. Alink and R. Dijkstra, Neth. Patent 69013.

funnel, fitted with a cotton filter. The precipitate is suspended in one litre of hydrochloric acid (2N), again filtered and washed with about one litre of distilled water and 400 ml of alcohol. The product is dried for 6 hours at 100° C. The yield is 540–560 g (57.5–59.5%) of white needles. The product decomposes at about 315° C before it melts. The compound is titrated with barium hydroxide and bromocresol purple as an indicator.

Found: Eq. wt. 203.
Calculated for $C_7H_8O_4NS$: Eq. wt. 203.

Nitration of 1-methyl-2-hydroxy-benzene-5-sulphonic acid with potassium nitrate.
Five hundred grams of o-cresol are sulfonated with 500 ml of concentrated sulphuric acid (sp. gr. 1.84), and the mixture poured into two litres of distilled water. The stirred solution is heated at 70° C and a warm solution of 465 g of potassium nitrate in two litres of distilled water is added. The temperature is kept at 70–75° C for 30 minutes. After slowly cooling, the potassium salt of III crystallizes, this then being filtered off and dried in air for 24 hours. The yield varies from 1000 to 2100 g but when dried at 100° C all the portions amount to about 750 g (60%). Analysis of the product after recrystallization and drying at 100° C shows K = 13.97%; calculated for $C_7H_6O_4NSK$: K = 14.41%.

The reduction of 1-methyl-2-hydroxy-3-nitrobenzene-5-sulphonic acid with sodium sulphide.

Fifty grams of o-cresol are sulfonated and nitrated as before and then 210 ml of a sodium hydroxide solution (40%) is added. A solution of 176 g $Na_2S \cdot 9H_2O$ in 66 ml of water is poured slowly into the hot alkaline solution of the nitro compound. The mixture is heated under reflux for two hours and after cooling poured into a two litre beaker, then being neutralized with 325 ml concentrated hydrochloric acid.

Some sulphur precipitates immediately and after twenty-four hours the amino compound together with the sulphur is collected on a Büchner funnel. The mixture is treated with 275 ml water and 50 ml of a 40% sodium-hydroxide solution. The sulphur is filtered off, the filtrate neutralized with 100 ml concentrated hydrochloric acid and the precipitated amino compound is collected on a filter, washed with water and alcohol and dried at 100° C.

The yield is 50 g (53%).

The reduction of 1-methyl-2-hydroxy-3-nitrobenzene-5-sulphonic acid with cast iron.

Fifty grams of o-cresol are sulfonated and nitrated in the known manner. This solution is diluted with 800 ml water and 275 ml concentrated hydrochloric acid (sp. gr. 1.19) and heated at 90° C while stirring. One hundred grams of degreased iron filings are added in small portions. After all the filings have been added 25 ml concentrated hydrochloric acid are poured in. After the gas evolution has ended the hot solution is very quickly filtered through a glass filter. Very soon the amino compound precipitates; it is filtered off, washed and dried at 100° C. The yield is 52 g (55%) of greyish white needles.

The electrolytical reduction of 1-methyl-2-hydroxy-3-nitrobenzene-5-sulphonic acid.

A rolled sheet is placed in a 500 ml porous jar and the jar filled up with 15% sulphuric acid. The jar is placed in a two litre beaker containing a graphite plate with a surface of 30 square cm. In the beaker are placed a nitrated mixture obtained from 18 g o-cresol, 20 ml $SnCl_2$ solution (67 g per 100 ml) and 80 ml concentrated hydrochloric acid, the beaker then being filled up to 400 ml with distilled water.

The lead sheet serves as anode and the graphite plate as cathode. With a tension

of 16 volts and a density of 6.5 A per dm² while stirring the liquid in the cathode room, the reduction is complete in 45 minutes at a temperature of 95° C. It is found that 5 g of tin have been precipitated on the cathode. The amino compound is filtered off, washed and dried at 100° C. The yield is 14.3 g (42 %).

Preparation of 1-methyl-2-hydroxy-3-diazobenzene-5-sulphonic acid.

250 g arsenic trioxide or 250 g starch and 800 ml nitric acid (sp. gr. 1.37) are put into a one litre round-bottomed flask, fitted with a reflux condenser attached to a drop-counter. The flask is slowly heated in a water bath and the gaseous nitrous anhydride formed is decanted into an 800 ml beaker containing 190 ml distilled water and 10 ml concentrated nitric acid (sp. gr. 1.37). The beaker is cooled with a mixture of ice and salt and its contents are kept at a temperature of -5 to 0° C. A few minutes after the gas has been admitted, 150 g of amino compound is added in small portions. The amino compound dissolves during diazotization and after some time the diazonium compound crystallizes. The rate of the gas flow is so regulated that the temperature does not rise above 5° C. When a sample entirely dissolves in water, the reaction has been completed (2½-6 hours). The beaker is then chilled in an ice-salt bath to -10° C and left at that temperature for one and a half hours. The solid diazonium compound is separated by filtration through a glass filter, then suspended in ice-cold alcohol, again filtered and dried in air. The yield is 120-130 g (65-70 %). The diazonium compound is titrated with barium hydroxide and bromocresol purple as an indicator in yellow light. The compound crystallizes into fine yellow needles mostly with 2 molecules of water but also with one molecule of water or none. In the air the crystal water gradually evaporates.

Found: Eq. wt. = 250.
Calculated for C₇H₆O₄N₂S · 2 H₂O: Eq. wt. = 250.

Preparation of the sodium salt of 1-methyl-2-hydroxy-3-diazobenzene-5-sulphonic acid.

400 ml water, 500 ml acetone, 600 g amino compound and 10 ml concentrated fluoboric acid are put into a three litre beaker. The suspension is mechanically stirred and kept at 20° C by cooling in a mixture of ice and salt after which a solution of 240 g sodium nitrite in 450 ml water is slowly added in the course of one hour. The temperature may not rise above 30° C. After all the nitrite solution has been added the mixture is cooled to 0° C. The compound is filtered off on a glass filter, transferred to a beaker, stirred with ice-cold alcohol and again collected on a glass filter. The sodium salt is dried in air and amounts to 750-775 g (78-80 %) of deep yellow plates.

Found: Na 6.92, 6.79; H₂O 28.19, 28.23.
Calc. for C₇H₅O₄N₂SNa · 5 H₂O: Na 7.05; H₂O 27.60.

Eindhoven, October 1951.

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