

Spectroscopic Measurements

The infrared spectra were measured on a two-beam prism UR-20 model spectrophotometer, in the $700-2000\text{ cm}^{-1}$ range (NaCl optics). The apparatus was calibrated using a polystyrene foil. The samples were prepared in nujol, 4 mg substance per 15 mg nujol.

Electronic spectra were measured on a prism Perkin-Elmer spectrophotometer, model 450, in 215–750 nm region, in methanol. Concentrations: $1 \cdot 10^{-3}\text{M}$, $1 \cdot 10^{-4}\text{M}$, $1 \cdot 5 \cdot 10^{-5}\text{M}$. Cell widths: 0.50 cm and 1.00 cm.

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**AROMATIC DIAZO
AND AZO COMPOUNDS. LXXXVII.*****FORMATION OF 3-BENZENEAZOPYRIDINE
FROM SULPHITE ADDUCT**

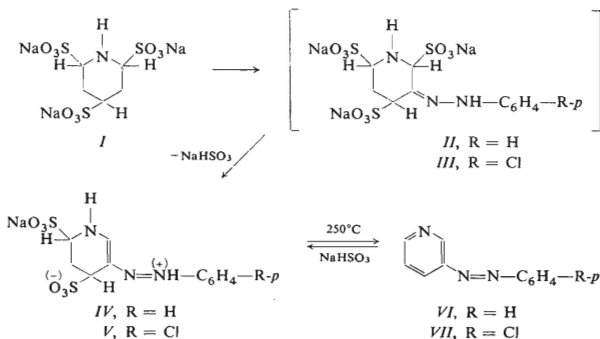
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Previously we described¹ the preparation of the azo compound *IV* which is formed by coupling benzenediazonium chloride with the adduct of pyridine and three molecules of sodium hydrogen sulphite (*I*), the azo compound *II* being probably formed first whereupon a rapid spontaneous splitting off of one sulphite molecule follows. The subject of the present paper is a study of splitting off of the two remaining sulphite molecules with the aim of obtaining 3-benzeneazopyridine (*VI*).

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SCHEME 1

The usual way of desulphitation *i.e.* heating of the azo compound **IV** with aqueous sodium carbonate at 100°C fails. Heating with aqueous sodium hydroxide gives the compound **VI**, the yields are, however, very low because a simultaneous deeper decomposition occurs. The reaction is best accomplished by heating the dry substance **IV** or its mixture with sodium carbonate *in vacuo*, whereupon the product **VI** distills immediately after its formation and it is thus preserved from decomposition. Yield: 43% of the product containing about 0.5% azobenzene and a small amount of an oily substance. 3-(4-Chlorobenzeneazo)pyridine was prepared in a similar way from the chlorinated azo dyestuff **V**. The structure of the both dyestuffs **VI** and **VII** was confirmed by reductive splitting whereupon 3-chloropyridine was formed along with aniline and *p*-chloroaniline respectively.

As it turned out, the above-mentioned desulphitations necessitate the use of the purest possible azo compound **IV**. The product which precipitates from the solution during synthesis or crystallization directly without sodium chloride addition fits well, whereas the fraction of the azo compound **IV** obtained from the filtrate after a sodium chloride addition gives only half yield of the substance **VI** which, in addition to it, remains mostly oily even after a long period.

The pyridine adduct is thus far more reactive than pyridine itself. We tried to use the adduct for further reactions. It turned out that the adduct **I** can be nitrated with a mixture of nitric and sulphuric acids at mere 20°C , whereas pyridine itself needs a temperature of 330°C (ref.²). The spontaneous desulphitation gives 3-nitropyridine. However, the yield is about 15% only which is similar to direct nitration of pyridine².

EXPERIMENTAL

The melting points were corrected with the use of comparison substances.

3-Benzeneazopyridine (**VI**)

10 g Sodium 3-benzeneazo-1,4,5,6-tetrahydropyridine-4,6-disulfonate (**IV**) (ref.¹) (the yields are lower when greater amounts are used) was mixed and ground with 10 g sodium carbonate and the mixture was introduced into a horizontal glass tube in such a way that a free channel remained

in the upper part of the tube for the gas flow. At the end of the tube a place for distillate collecting was separated by the two barriers made by pushing the glass walls inside. The mixture was heated quickly at 260°C in the vacuum of water pump under a slow stream of carbon dioxide. The oil distills during the heating already and solidifies after cooling and inoculation; yield 1.9 g (43%). The product *VI* was freed from a small amount of oil by suction and again distilled; it solidified immediately during distillation. The middle part of the cake was dried *in vacuo* at 20°C over sodium hydroxide and sulphuric acid and analysed. For $C_{11}H_9N_3$ (183.2) calculated: 72.11% C, 4.95% H, 22.94% N; found: 72.03% C, 5.02% H, 22.66% N. The substance can be crystallized from half a volume of ethanol and gives yellow plates. The crystallization does not, however, remove the azobenzene present (about 0.5%). Its content was estimated by chromatographic comparison (Whatman paper No 1; butanol saturated with 2.5M-HCl) of its sample, submitted to the benzidine rearrangement by action of stannous chloride and hydrochloric acid, with a series of the standards prepared similarly from authentic azobenzene. The content of azobenzene in the substance *VI* was lowered to about 0.01% by means of alumina column chromatography using chloroform as eluent. The product melts at 50°C. Its reduction with zinc powder in aqueous ethanolic ammonia gives aniline and 3-aminopyridine which was proved by comparison with the respective authentic substances on paper chromatogram. The substance *VI* dissolves in organic solvents to pale yellow solution; it is insoluble in water, however slightly soluble after addition of strong acids. On heating with aqueous sodium hydrogen sulphite it gives an intensively yellow dyestuff which is identical with the original dyestuff *IV*.

3-(4-Chlorobenzeneazo)pyridine (*VII*)

It was prepared from the chloro derivative *V* analogously to the substance *VI*. It forms yellow needles, m.p. 98°C (ethanol). For $C_{11}H_8ClN_3$ (217.7) calculated: 60.70% C, 3.70% H; found: 60.07% C, 3.98% H.

Nitration of the Pyridine Adduct

0.5 g Pyridine adduct (*I*) was dissolved in 2 ml 98% H_2SO_4 at 20°C and nitrated with 0.4 ml (5 equivalents) 71% HNO_3 . After 12 days standing the volume of the mixture was adjusted at 25 ml with water. The content of the product was estimated semi-quantitatively (after reduction with zinc powder and hydrochloric acid) by means of chromatographic comparison with a standard series of 3-aminopyridine. The yield of 3-aminopyridine and hence 3-nitropyridine is about 15%. Not even traces of the nitro and amino derivatives were formed in an analogous experiment using an equivalent amount of pyridine instead of its adduct.

DISCUSSION

The three molecules of sodium hydrogen sulphite are split off from the primary coupling product *II* with unequal readiness. The first molecule splits off spontaneously during the coupling at 15°C already, the remaining two split off with extraordinary difficulties, only at 250°C. Obviously, this considerable difference is caused by the high stability of the disulphitated azo compound *IV* which possesses a perfectly conjugated system. The same fact causes probably the resistance of the azo compound *V* towards reduction in acid medium¹.

The whole reaction sequence — addition of sodium hydrogen sulphite to pyridine³, diazo coupling of the adduct¹ or its nitration, and splitting off of the all sulphite — show the main characteristics of Bucherer reactions: facilitation or aromatic substitution by acid sulphites. The term Bucherer reaction usually denotes a substitution of amino group by hydroxyl or *vice*

versa in the presence of acid sulphites which accelerate these reaction by several orders of magnitude. These reactions consist of *a*) primary addition of an acid sulphite to the substrate, *b*) proper aromatic substitution, and *c*) reverse splitting off of the sulphite. In several cases the sulphite adducts could also be isolated which is, however, not usually done. In contrast to this, the intermediate isolation of sulphite adduct is necessary in the case of the reactions described by us because the remaining sulphites must be removed, otherwise diazonium salts or nitric acid would react with sulphites more rapidly than with the substrate. Besides that the diazo coupling must be carried out at a considerably lower temperature than that necessary for the addition, otherwise the diazo compound would be completely decomposed. The same reason applies for the fact that pyridine can be submitted to direct nitration but not to diazo coupling. Direct nitration can be forced by an increased temperature² whereas the coupling cannot as the diazo compounds decompose at higher temperatures.

It is a paradox that the addition of acid sulphite to a substrate facilitates nucleophilic reactions (hydrolyses, amonolyses) in some cases by several orders of magnitude, and, on the contrary, electrophilic reactions (diazo couplings, nitrations) in the cases described by us. We, therefore, suppose that in the latter cases, too, a nucleophilic reaction takes place first, *i.e.* a splitting off of the proton, the anion thus formed reacts in a rapid subsequent reaction with diazonium or nitronium cation.

The elemental analyses were carried out by Mrs J. Jičinská, V. Kudýnová, Z. Marešová, and H. Šmahelová under the supervision of Dr L. Synek in the Analytical-Physical Department of our Institute.

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