

AROMATIC DIAZO AND AZO COMPOUNDS. LXXXVI.\*  
DIAZO COUPLING WITH BUCHERER ADDUCT OF PYRIDINE

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The adduct of pyridine and three molecules of sodium hydrogen sulphite couples with benzene-diazonium chloride to give the yellow dyestuff *II* of the polymethine type. Further, very small amounts of a yellow and yellowish red dyestuffs are formed corresponding most probably to *V* and *VI* respectively.

Recently we found<sup>1</sup> that the adduct of resorcinol and three molecules of sodium hydrogen sulphite couples with diazonium salts. As the hydroxyl groups present in the adduct are not connected conjugatively with the coupling site, we presumed that the activation was due to two strongly electron-attracting sulfonic acid groups on the neighbouring carbon atoms. Up to that time only diazo couplings on a carbon atom directly carrying a sulfonic acid or nitro group were known<sup>2</sup>; their mechanism can be supposed to consist of the splitting off of the proton from the carbon atom and subsequent reaction of the anion formed with diazonium cation. If the presumption concerning the activation of the resorcinol adduct is correct, then, of course, even analogous compounds without hydroxyl groups should couple, e.g. pyridine adduct with three molecules of sodium hydrogen sulphite. According to the present knowledge about other Bucherer adducts, this compound, obviously, has not the structure of sulphite esters originally suggested; more probably it corresponds to sodium piperidine-2,4,6-trisulfonate(*I*), even though there is not yet any unambiguous experimental evidence for it. We have found that this adduct does couple with diazonium compound which is the subject of the present paper.

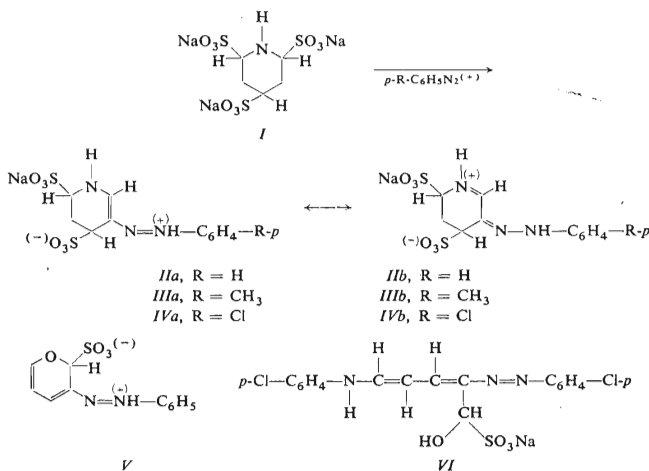
Bucherer and Schenkel<sup>3</sup> carried out the addition by heating pyridine with sodium hydrogen

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sulphite solution. After neutralization they removed the excess sulphite by addition of barium iodide and precipitated the product *I* with ethanol. We have found that the isolation can be simplified by lowering the water amount in the synthesis whereupon a greater part of the adduct *I* precipitates from the solution during the reaction already.

Slightly electrophilic diazo compounds do not practically couple with the adduct *I* whereas, of course, strongly electrophilic diazonium compounds (nitro or sulfo derivatives) couple rapidly, but they give only mixtures of dyestuffs under various conditions. Satisfactory results are obtained with medium electrophilic diazo compounds such as benzenediazonium chloride and its methyl or chloro derivatives. Slow addition of these diazo compounds to the adduct gives, besides the diazo decomposition product, an almost homogeneous coupling product, a well soluble intensive brilliant greenish yellow *II* or its methyl or chloro derivatives *III* and *IV* respectively.

In our first experiments the yields of the main coupling product *II* (resp. *III* or *IV*) were about 10% only, and the product could be precipitated from the solution only with difficulties by addition of sodium or potassium chloride. Probably, a decomposition of the diazonium salt by liberated or residual sulphites occurred. A calcium carbonate addition to the coupling mixture precipitates the sulphites as calcium salt, the yields of the compound *II* increase to about 70%, and the product precipitates from the solution during the reaction already.



SCHEME 1

The coupling takes place in the position 3 of the nucleus which follows from the identity of the products of the reduction splitting of the dyestuffs *II–IV*; the reduction proceeds readily with zinc dust in ammonia medium. In all the cases 3-aminopyridine is formed along with the respective initial amin – aniline resp. its methyl or chloro derivative, *i.e.* desulphitation takes place simultaneously. The structure of the dyestuffs *II–IV* is supported by colour reactions too (they are intensive brilliant greenish yellows in acid medium whereas practically colourless in alkaline medium) which are similar to the reactions of other simple polymethine dyestuffs having a conjugated chain of a similar length. Absorption curves of the compound *II* in acid and alkaline media are very similar, the latter being shifted towards the ultra-violet region. Obviously, this hypsochromic shift in alkaline medium is caused by a decrease of symmetry and (hence) conjugation of the colour centre due to splitting off of the proton, as it is the case with other polymethine dyestuffs, too. From the elemental analysis it follows that the coupling is connected with a spontaneous splitting off of one of the sulphite molecules. The sulfonic acid group in the position 2 splits off because a conjugated chromophoric system can be formed in this way only. The readiness of the splitting off of one sulphite molecule can be explained by the considerable stability increase of the molecule due to the formation of the abovementioned conjugated system.

The compounds *II–IV* show a behaviour not usually encountered with azo dyestuffs: they are not reduced in acid medium *e.g.* diluted hydrochloric acid even after several hours heating at 100°C with such reagents as stannous chloride or sodium sulphite. This property was useful for purification of the compound *II*; all the side dyestuffs originating from the diazo decomposition were reduced by the action of hot sulphite solution. The resistance of the compound *II* towards reduction in acid medium can be explained by conjugation and stabilization. The compounds *II–IV* can be taken to be azo as well as polymethine dyestuffs. As they can be prepared by a simple diazo coupling, they belong to the most readily accessible polymethine dyestuffs.

The reaction of benzenediazonium chloride with the adduct *I* gives (besides the main product *II* and the diazo decomposition products) very small amounts of two further coupling products: a slightly soluble yellow and a yellowish red. The elemental analysis proved that the yellow by-product has one sulfonic acid group only which could already be anticipated from its slight solubility in acid medium. Colour reactions of this by-product are almost the same as those of the main product *II*, except for a somewhat lower brilliancy, and it is, therefore, very surprising that the by-product contains two nitrogen atoms only. With respect to its close analogy to the compound *II*, it can possibly possess the structure *V* which is not yet settled.

The amount of the second by-product increases with the electrophility of diazo compound and its excess in coupling reaction mixture. The latter dependence stands in accord with the fact that the amount of the by-product formed is smaller when diazo

component is added gradually during the reaction than in the reverse arrangement when all the diazo component is present at the beginning. Thus the yellowish red is formed in traces only on gradual addition of *p*-methylbenzenediazonium chloride. On the contrary, the yellowish red forms a marked spot in paper chromatogram when the more electrophilic *p*-chlorobenzenediazonium chloride and the conditions of reverse addition are adopted. These conditions were used for preparation of the by-product. The results of elemental analysis are not straightforward and the structure is not yet fully understood. From the nitrogen content it follows that two reactions with *p*-chlorobenzenediazonium chloride took place probably, the one being a diazo coupling reaction and the other an arylation reaction with splitting off of the nitrogen. The arylation obviously causes a ring opening of pyridine which is also suggested by a strong bathochromic shift and entirely different colour reactions as compared to the compounds II–V. We suggest the structure VI as a probable possibility. Its formation consists most probably in coupling of the adduct I in the position 3 and subsequent stabilization by splitting off of the proton. If the diazo compound is present in a great excess at this moment, an at least partial arylation of nitrogen takes place which causes a ring opening and formation of the compound VI. If an excess of the diazo compound is not present, further stabilization takes place by splitting off of one sulphite molecule to give the compound II which does not react further.

## EXPERIMENTAL

If not otherwise stated, the substances for elemental analyses were dried at 120°C in the vacuum of water pump 2 hours. The paper chromatography was carried out in a descending arrangement.

### Preparation of Pyridine Bucherer Adduct

A mixture of 1450 ml water, 396 g (5 mol) pyridine and 850 g (4.5 mol) sodium pyrosulphite was refluxed (96°C) with stirring 26 hours then further 860 g sodium pyrosulphite was added and refluxing continued 20 hours. At the end the product separated in such a way that the mixture could just be stirred. The mixture was left to cool overnight at 20°C and the white prisms of the adduct I precipitated were collected by suction and dried at 20°C. The yield was 1280 g of the product containing 12.4% C, *i.e.* 53%. 1310 ml filtrate gave further 500 g product (second fraction, 17%) on addition of 260 g sodium chloride.

### Diazo Coupling with Pyridine Bucherer Adduct

600 ml cold 2.5M-NaNO<sub>2</sub> was added to a mixture of 140 g (1.5 mol) aniline, 750 ml 5M-HCl and 750 g ice so that the temperature did not exceed 15°C. After 20 minutes at 5°C, the excess nitrous acid was removed by addition of sulphamic acid. 485 g of pyridine adduct containing 12.4% C (*i.e.* 1 mol) was added to 500 ml benzenediazonium chloride solution and the acid present was neutralized immediately with an excess of calcium carbonate. The remaining diazonium salt was added during 0.5 hour at 15°C with simultaneous neutralization of the reaction mixture with calcium carbonate (total 280 g). 4.5 Hours after the beginning of coupling reaction,

the mixture became thick with the precipitated product, but it still contained excess diazonium salt. The mixture was left to stand overnight whereupon the diazo compound disappeared. A sample was chromatographed on the paper Whatman No 4 using water-acetic acid-pyridine-isoamyl alcohol 1 : 1 : 2 : 2 mixture as eluent: the main product forms a greenish yellow spot  $R_F$  0.45 and the coupling by-products form two very weak spots (which are visible only in appropriately concentrated samples) greenish yellow  $R_F$  0.55 and yellowish red  $R_F$  0.6. At the solvent front of the chromatogram there is a brown spot of the diazo decomposition products; the respective comparison sample was prepared by neutralization of a small portion of the diazo solution with excess calcium carbonate and leaving to stand overnight. The reaction mixture was acidified with 350 ml 36% HCl (Congo Red), heated at 87°C and filtered (Filtrate A). The precipitate was mixed with 500 ml water, acidified with hydrochloric acid (Congo Red) and again filtered (Precipitate A, Filtrate B). Combined filtrates A and B gave yellow needles of the dyestuff *II* on cooling. They were collected by suction and dried to give 120 g product. The mother liquor was treated with sodium chloride to give further 162 g dyestuff *II*. According to colourimetric analysis, the filtrate still contains 27 g of the dyestuff *II*, so that the overall yield is 309 g (70%).

The dyestuff *II* was purified by dissolving in water, the solution was slightly (Congo Red) acidified with hydrochloric acid, a small amount of pyrosulphite was added and the mixture was heated to boiling until it became light and transparent. The sodium chloride was added (5% by volume) and the mixture was cooled overnight and filtered (Precipitate B). The dyestuff *II* was precipitated by addition of further sodium chloride (10%) to the filtrate and collected by suction on the subsequent day. For elemental analysis 0.3 g of the dyestuff *II* was dissolved in 2 ml water, acidified with two drops of 2.5M-HCl and 2 ml aqueous solution containing 0.17 g  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$  was added; the mixture was filtered the day after and the dyestuff *II* was precipitated from the filtrate by addition of 5 volumes of ethanol, collected by suction and washed with 80% ethanol. For  $\text{C}_{11}\text{H}_{11}\text{BaN}_3\text{O}_6\text{S}_2 \cdot 2.5 \text{H}_2\text{O}$  (527.7) calculated: 25.04% C, 3.05% H, 26.02% Ba, 7.96% N, 12.15% S; found: 25.45% C, 2.88% H, 25.95% Ba, 7.81% N, 12.18% S.

The coupling reactions with diazotized *p*-aminotoluene and *p*-chloroaniline were carried out in a similar way, sodium carbonate being used instead of calcium carbonate. The yield was about 10%. The dyestuffs were precipitated with potassium chloride and for analysis recrystallized from a water-acetone mixture (1 : 1). For  $\text{C}_{12}\text{H}_{14}\text{KN}_3\text{O}_6\text{S}_2$  (399.5) (*III*) calculated: 36.08% C, 3.53% H, 9.79% K, 10.52% N, 16.05% S; found: 36.64% C, 3.57% H, 9.48% K, 10.55% N, 15.84% S. For  $\text{C}_{11}\text{H}_{11}\text{ClKN}_3\text{O}_6\text{S}_2$  (419.9) (*IV*) calculated: 31.46% C, 2.64% H, 8.44% Cl, 9.31% K, 10.01% N, 15.27% S; found: 32.01% C, 2.87% H, 8.88% Cl, 8.80% K, 10.14% N, 15.47% S.

**Reduction:** The dyestuffs *II-IV* were dissolved in 25%  $\text{NH}_3$  and shaken with zinc powder until decolorization (several seconds). The solutions obtained were chromatographed (on paper Whatman No 1 using butanol saturated with 2.5M-HCl as eluent) along with authentic substances. The spots were made visible by diazotization and coupling with 2-naphthol-3,6-disulfonic acid in ammonia medium. In all the three cases an intensive redish yellow spot of 3-aminopyridine was found along with red spots of the respective amines — aniline, *p*-aminotoluene or *p*-chloroaniline.

**Isolation of the dyestuff V:** The precipitates A and B (see above) obtained from 1 mol of the pyridine adduct were combined and heated with water under simultaneous alkalization with sodium carbonate. The insoluble substances formed by the diazo decomposition were removed by hot filtration. The dyestuff *V* which was precipitated from the filtrate by addition of sodium chloride (5% by volume) is almost homogeneous chromatographically. Yield 0.3 g. The dyestuff was purified for analysis by dissolving in 25 ml water at 75°C under slight alkalization with 1.25M- $\text{Na}_2\text{CO}_3$  (several drops) using Brilliant Yellow paper indicator, the solution was filtered and acidified (warm) with 36% hydrochloric acid (five drops) until a slight reaction of Congo Red.

The yellow prisms precipitated on cooling were collected by suction, washed and dried. For  $C_{11}H_{10}N_2O_4S$  (266.3) calculated: 49.62% C, 3.78% H, 10.52% N, 12.04% S; found: 49.53% C, 4.51% H, 9.28% N, 12.57% S, Na negative.

#### Isolation of Yellowish Red By-Product VI

38.1 g (0.3 mol) *p*-chloroaniline was diazotized by usual method (10°C, volume 420 ml), and then 15 ml acetic acid and 48.5 g (0.1 mol) pyridine adduct were added. The mixture was stirred until disappearance of the diazo compound (30 hours) under continuous neutralization of acid with sodium carbonate (slight reaction of Congo Red) and the precipitate was collected by suction. The solid substance contains mainly the decomposed diazo compound and the whole red product too. The mixture was dissolved in 150 ml pyridine and 85 g alumina was added to the solution. The alumina with adsorbed by-product was collected by suction, washed with pyridine and ethanol, dried and then extracted with water. The extract was evaporated *in vacuo* until dry (2 g). The residue was mixed with 40 ml water, filtered and the dyestuff was precipitated with sodium chloride (10% by volume), yield 0.3 g. For analysis the substance was purified by dissolving in 6 ml water, acidification with one drop of acetic acid and reprecipitation with a solution of 0.2 g  $BaCl_2 \cdot 2 H_2O$  in 6 ml water. The amorphous brown-red precipitate of the compound VI was collected by suction and dried. For  $C_{34}H_{28}BaCl_4N_6O_8S_2 \cdot 5 H_2O$  (1082) calculated: 37.74% C, 3.54% H, 12.69% Ba, 13.11% Cl, 7.77% N; found: 37.52% C, 3.02% H, 11.37% Ba, 13.02% Cl, 7.79% N.

*The elemental analyses were carried out by Mrs J. Jičínská, V. Kudýnová, Z. Marešová, E. Ne-kvapilová M. Skutilová, H. Šmahová and Mr Z. Netušil under the supervision of Dr L. Synek in the Analytical-Physical Department of our Institute.*

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