BENZIDINE REARRANGEMENT. VI.*

REDUCTION AND REARRANGEMENT OF 3-BENZENEAZOPYRIDINE

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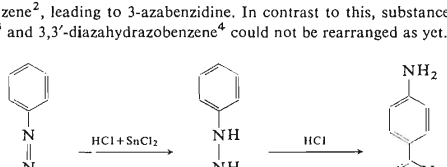
In the preceding communication[1] we described how 3-benzeneazopyridine on reduction with zinc in 20% ammonia gives rise to aniline and 3-aminopyridine. The present paper is devoted to the reduction of the same compound in acid medium, during which predominantly 2-azabenzidine is formed as the endproduct. In the literature a similar rearrangement is described only for 2-azahydrazobenzene[2], leading to 3-azabenzidine. In contrast to this, substances such as 4-azahydrazobenzene[3] and 3,3'-diazahydrazobenzene[4] could not be rearranged as yet.



I *II* *III*

On reduction of a solution of 3-benzeneazopyridine (*I*) with stannous chloride in hydrochloric acid at 20°C a weakly soluble salt of chlorostannic acid with 2-azahydrazobenzene (*II*) is first precipitated from the solution. Its structure follows from the fact that on further treatment with hydrochloric acid, especially under warmth, it dissolves gradually and affords the same decomposition products, and in the same proportion as starting 3-benzeneazopyridine (*I*). With other azobenzene derivatives the intermediate hydrazobenzenes usually do not separate from the solution and they rearrange rapidly. In the case of azaderivative *II* the possibility of isolation is caused both by lower reactivity of this compound, and by the low solubility of its complex salt with chlorostannic acid. The last mentioned property is characteristic of some other pyridine derivatives as well. Chlorostannate of 2-azahydrazobenzene (*II*) dissolves in warm hydrochloric acid slowly. On control paper chromatograms appear after detection by diazotation and coupling with 2-naphthol-3,6-disulfonic acid several characteristic spots. The main product is 2-azabenzidine (*III*). It was isolated on a preparative scale and identified by elemental analysis. The fact that it belongs to the benzidine group is indicated by its lowest solubility and also highest bathochromic shift as compared with all other substances present or spots detected on chromatograms. The structure of another substance — *x*-azadiphenyline, which is formed

* We consider the following papers in This Journal as parts I—V of this series: *29*, 531 and 752 (1964); *31*, 3555 and 4129 (1966); *32*, 2882 (1967), and in Tetrahedron Letters: *1966*, 4955. The present paper represents at the same time part LXXXVIII of the series "Aromatic diazo- and azo compounds".

in approx. 20—30% yield (with respect to the present azabenzidine), is proposed on the basis of its appreciable similarity with the homocyclic diphenyline. It gives a similar hue after detection and the distance of its spot from the corresponding benzidine derivative is almost identical. However, it is not known which of the three possible isomeric azadiphenylines it is.

Other formed substances were identified by chromatographic comparison with authentic preparations. These are 3-aminopyridine, aniline, and a series of various chloro derivatives. *p*-Chloroaniline in particular belongs here, the spot of which is stronger than that of aniline. 2-Chloroaniline, 2,4-dichloroaniline, *x*-chloro-3-aminopyridine, give weaker spots, while the spot of *x*-chloro-2-azabenzidine is weakest. The standards of the two last mentioned substances were prepared by chlorination of the basic compounds with a small amount of the chlorinating agent in acid medium. We did not try to identify the positions of chlorine in them. 3-Benzeneazopyridine (*I*) could not be detected on the chromatogram. However, it gives only weak spots, and it is possible that it escaped our attention.

All these substances which we found are also formed from 3-benzeneazopyridine on reduction in acid medium under simultaneous rearrangement. The presence of stannous chloride during the rearrangement does not suppress the formation of chlorinated derivatives. The lowering of the concertation of hydrochloric acid from 12M to 2·5M during the rearrangement brings about a decrease in the amount of the chlorinated substances, which is most manifest in the case of *x*-chloro-3-aminopyridine and *x*-azasemidine, while the amount of azabenzidine slightly increases. We also looked for chlorinated products during the reduction and the rearrangement of homocyclic azobenzene. We found that in strongly acid medium a very small amount of 4-chloroaniline is formed in addition to aniline. However, this amount is much lower than in the case of the heterocyclic compound *II*, *i.e.*, at a guess, much lower than 1%. The formation of 4-chloroaniline is mentioned in recent literature[5] in connection with the reduction of azobenzene with isopropyl alcohol and hydrochloric acid.

On comparison of the rearrangement of the heterocyclic hydrazo derivative *II* with hydrazobenzene it is evident that they do not differ appreciably with respect to the ratio of the formed benzidine and semidine. In both cases this ratio decreases to a certain extent with the concentration of hydrochloric acid and with the temperature. However, in the case of the heterocyclic compound *II* a much greater disproportionation takes place, shown by the formation of a much larger amount of formed monoamines. The mode of disproportionation is also different. In the heterocyclic series mainly chloro derivatives are formed as oxidation products.

EXPERIMENTAL

3-Azahydrazobenzene (*II*)

To a solution of 3-benzeneazopyridine (*I*, 1·5 g) in 2·5M HCl (5 ml) a solution of $SnCl_2.2\,H_2O$ (2·1 g) in 2·5M-HCl (5 ml) was added at 70°C. Both solutions were filtered before mixing. Greyish globular precipitate was formed which was filtered off under suction, washed with water, acidified with hydrochloric acid, dried over sodium hydroxide and conc. sulfuric acid for two days, and at 100°C *in vacuo* for an additional 2 hours. For $2\,C_{11}H_{11}N_3.H_2SnCl_6$ (703·9) calculated: 37·54% C, 3·44% H, 11·94% N, 16·86% Sn; found: 37·77% C, 3·57% H, 11·80% N, 17·56% Sn.

2-Azabenzidine (*III*)

$SnCl_2.2\,H_2O$ (12·4 g), 2·5M-HCl (150 ml), and 3-benzeneazopyridine (*I*, 3 g) were mixed and heated under reflux for 15 minutes. Aliquot A was taken out and the remaining, main part of the reaction mixture was evaporated to a syrupy consistence *in vacuo*. The material solidified in the cold. It was crystallised in 30 ml of boiling butanol, giving needles which were filtered off with

suction and washed with a small amount of butanol. Yield, 2·1 g. The material was dissolved in water (10 ml) and the base set free on addition of sodium carbonate at 50°C. After cooling the base was filtered off and then freed from the remaining tin by dissolution in hot ethanol (15 ml) and setting aside overnight. The solution was filtered again and the filtrate was evaporated to dryness, and the substance was crystallised from water (40 ml); m.p. 186°C (corr.). The product was dried *in vacuo* at 120°C for 2 hours. For $C_{11}H_{11}N_3$ (185·2) calculated: 22·69% N; found: 22·42% N.

Identification of other reaction products: Aliquot A (see above) was chromatographed on Whatman No 1 paper in 1-butanol saturated with 2·5M-HCl. After drying the chromatogram was detected by exposure to nitrous gases, spraying with a solution of sodium 2-naphthol-3,6-disulfonate, and alkalization with ammonia. Nine spots appeared on the chromatogram. At R_F 0·1 a blue spot could be detected after 2 hours heating of the sample, when the spot of substance *III* was already weak. The composition is unknown. At R_F 0·2 the main spot appeared, distinctly violet, corresponding to 2-azabenzidine (*III*). At R_F 0·3 a red-orange spot was detected, 3—5 times weaker than the main spot. Its hue was similar to that of diphenyline. The ratio of intensities and the difference of R_F values (with respect to the main spot) are analogous to the differences between diphenyline and benzidine. An intensively yellow-orange spot is located at R_F 0·4 which according to its comparison with an authentic sample is due to 3-aminopyridine. At R_F 0·5 to 0·6 weaker spots were present: violet and yellowish-orange. According to chromatographic comparison these substances are identical with the products of chlorination of 2-azabenzidine or 3-aminopyridine, which were obtained by dissolution of both substances in dilute hydrochloric acid and addition of chlorine water in several portions. At R_F 0·85, 0·9, 0·95 and almost 1·0 the following spots were detected: yellow-red (medium strength), orange (weak), red (intense), and blue-red (weak). Comparison with standards indicates that they are identical with aniline, 2-chloroaniline, 4-chloroaniline, and 2,4-dichloroaniline. 2-Azabenzidine, giving only a weak spot could not be detected.

A similar rearrangement was also carried out in conc. hydrochloric acid. Further experiments were carried out with 3-azahydrazobenzene *II*, both with and without the addition of stannous chloride.

Rearrangement of Azobenzene

A solution of azobenzene (0·1 g) in dioxan (5 ml) was pipeted in 1 ml portions. To each aliquot $SnCl_2.2\,H_2O$ (0·1 g) was added, in the first case dissolved in water (3 ml), and in other cases in 0·5M, 2·5M, and 10M-HCl (3 ml in each case). The mixtures were shaken and heated until decolorized, and then chromatographed as above. In addition to the products of rearrangement, those of disproportionation were also observed, namely aniline and traces of 4-chloroaniline. The amount of the latter compound increased with increasing hydrochloric acid concentration, but the compound was absent in the experiment carried out in pure water.

Elemental analyses were carried out by Mrs J. Jičínská, Mrs Z. Marešová, Mrs V. Kudýnová, Mrs H. Šmahelová, and Mr Z. Netušil, under the direction of Mr L. Synek, and by Mr Z. Jelínek under the direction of Mr J. Pikhart, in the analytical-physical laboratory of our Institute.

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ARYL- UND ARALKYLFERROCENYLMETHYLSULFIDE UND -SULFONE

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In der Literatur wurden bisher bloß verschiedene Verfahren zur Darstellung von Alkylferrocenylmethylsulfiden beschrieben, wobei auch die Zersetzung von Ferrocenylmethyltrimethylammoniumjodid in Gegenwart von wäßriger Natriumsulfidlösung angewendet wurde[1]. In der vorliegenden Mitteilung beschreiben wir die neue Darstellung der Aryl- und Aralkylferrocenylmethylsulfide und -sulfone (Tab. I) durch Reaktion von Ferrocenylmethyltrimethylammoniumjodid mit Thiophenolen in alkalischem Milieu bzw. mit Arylsulfinsäure-Alkalisalzen. Diese Methode ist einfach und liefert gute Ausbeuten.

Wir versuchten die Oxydation der bereiteten Sulfide zu den Sulfonen unter Anwendung von 30%igem Wasserstoffperoxid oder auch aktiviertem Braunstein und fanden, daß bei der Oxydation mit diesen Oxydationsmitteln augenblicklich Spaltung der Bindung zwischen Eisen und den Cyclopentadienylringen eintritt (Abscheidung von $Fe(OH)_3$).

Die Struktur der synthetisierten Verbindungen wurde durch die Elementaranalyse und die IR- und UV-Spektren nachgewiesen. In den IR-Spektren dieser Substanzen treten Banden auf, die den unsubstituierten Cyclopentadienylring charakterisieren (ω_{18} und ω_{10}) und ferner Banden, die den funktionellen Gruppen zugeordnet sind (Tab. II). Im ultravioletten Spektralbereich (200–340 nm) beobachtet man in den Absorptionsspektren 1–3 Maxima, die sich sehr schwer durch einen Übergang zuordnen lassen[2] (Tab. II). Im sichtbaren Spektralgebiet beobachtet man bei den meisten Derivaten eine Bande bei 440 nm ($\log \varepsilon$ 2,18), die dem Ferrocen-Chromophor zukommt (d-d-Übergang)[2].

EXPERIMENTELLER TEIL

Angewandte Substanzen und Verfahren

Thiophenol, Benzylmercaptan und die Benzol- und *p*-Toluolsulfinsäure-Natriumsalze waren handelsübliche Chemikalien; nach Literaturverfahren wurden *p*-Methylthiophenol[3], *p*-Chlor- und *p*-Bromthiophenol[4], *p*-Nitrothiophenol[5], *p*-Acetamidobenzolsulfinsäure[6] und Ferrocenyl-