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Abstract

Full Text

Chemistry

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ON THE INTERACTION OF NITROBENZENEDIAZONIUM BOROFLUORIDES WITH PHOSPHORUS TRICHLORIDE

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Whereas *m*- and *p*-nitrobenzenephosphonic acids can be synthesized by the Doak and Freedman diazo method without particular difficulty $^{(1-3)}$, the *o*-isomer cannot be obtained in this way $^{(4)}$. Our experiments confirmed these data. At the same time, in studying the correspondingly treated reaction mass, in which we presumed the presence of *o*-nitrobenzenephosphonic acid, a compound capable of being diazotized was discovered quite unexpectedly. From this diazo compound (without isolating it) it proved possible to obtain an azo compound (with 1-naphthol-4-sulfonic acid), investigation of which showed that it is a mixture of two azo dyes: one of them is the coupling product of chloroaniline, and the other that of an amine containing chlorine and a phosphonic group. In order to isolate this amine itself, i.e., chloroaminobenzenephosphonic acid, we decided to try to make use of its presumed ability to give sparingly soluble complexes with heavy metals, the formation of which was to be ensured by the ortho arrangement of the phosphonic and amino groups. Indeed, it was possible to isolate the corresponding copper complex, after decomposition of which 2-aminochlorobenzenephosphonic acid (I) was obtained in a chemically pure state.

The position of the chlorine in (I) was established by identifying 2-oxychlorobenzenephosphonic acid, obtained from (I) by replacing the amino group with hydroxy, with 2-hydroxy-5-chlorobenzenephosphonic acid isolated from its potassium salt. The melting point of a mixed sample of the two specimens showed no appreciable depression.

Investigation of the conditions favoring the formation and isolation of the new amine showed that, for this purpose, it was necessary to increase the amount of phosphorus trichloride 3.5-fold and that of copper 5-fold in comparison with the typical amounts recommended for carrying out the Doak and Freedman reaction $^{(4)}$.

The increase in the amount of copper, initially undertaken only to facilitate isolation of the amine, at the same time affected the final result of the reaction.

At a molar-atomic ratio of *o*-nitrobenzenediazonium borofluoride to copper of 1 : 1 (at a ratio to PCl_3 of 1 : 3.5), an amine was obtained in 15% yield (of which 5% was in the form of dye), whereas at a ratio of 1 : 0.2 the amount of amine is appreciably reduced (to 5%), but instead a substance is formed in 12-15% yield, investigation of whose properties and composition showed that it is the azo compound (II)

$$\overset{NH_2}{\text{benzene ring substituted by } PO_3H_2 \text{ and } Cl} \quad (I), \qquad Cl{-}C_6H_3(PO_3H_2){-}N{=}N{-}C_6H_3(PO_3H_2){-}Cl \quad (II)$$

The correctness of this formula (II) is confirmed not only by analysis, but also by the fact that reduction of the isolated substance gives 2-amino-5-chlorobenzolphosphonic acid.

In all cases in which the reaction was carried out, the formation of a small amount of nitrophenol was established, as well as chloroaniline, which was isolated in the form of a salt of acid (I).

Further investigation showed that the formation of amines and the chlorination process under conditions close to those of the synthesis of (I) also occur in the case of its isomers (see Table 1), i.e., they are of a general character, although with different degrees of completeness. It should be noted here that, in accordance with what was said above, the synthesized amines could be isolated through the copper complex only in the case of the *o*-isomer; the *m*- and *p*-isomers have not yet been isolated as such, but were obtained only in the form of azo dyes with resorcinol.

Table 1

Dependence of the amine yield on the ratio of diazonium borofluorides and nitrobenzene to phosphorus trichloride (in moles)

Compound	Amine yield, %	Amine yield, %	Degree of chlorination, %
	1:1	1:3.5	
Borofluoride of *o*-nitrobenzenediazonium	Traces	15	100
Borofluoride of *p*-nitrobenzenediazonium	2–2.5	30–35	15–20
Borofluoride of *m*-nitrobenzenediazonium	Traces	10–15	15–20
Nitrobenzene	Not detected	2–5	0

Additional experiments with nitrobenzene also showed the possibility of formation of a certain amount of aniline, i.e., in this case as well a process of reduction of the nitro group is observed, although with a low yield.

Thus, we have established for the first time that, depending on the ratio of the reacting substances and the so-called "catalyst," the interaction between nitrobenzenediazonium borofluorides and phosphorus trichloride can proceed at once in three mutually interwoven directions: 1) formation of a phosphonic group, 2) reduction of the nitro group, and 3) chlorination.

The last reaction proceeds most completely for the ortho isomer.

Experimental part*

To a mixture of 635 ml of abs. ethyl acetate with 155 ml (1.75 mole) of phosphorus trichloride and 25 g of cuprous chloride at 30° there is added, in small portions, a mixture of 118.5 g (0.5 mole) of the corresponding diazonium borofluoride with 25 g of cuprous chloride; as the addition proceeds the temperature rises and evolution of nitrogen begins. Care is taken that the temperature does not exceed 60°. After the evolution of nitrogen has ceased, the mass is kept at the same temperature for 3 hours. Then, at 15–35°, 10 ml of water is added very carefully to the reaction mass and it is heated at 50–65° for 1 hour. Then, at a temperature not above 45–60°, 590 ml of water is added.

In the case of the *o*-isomer, the reaction mass is neutralized with sodium carbonate to pH 4–5, heated to 45°, and, after cooling, the precipitated copper complex is filtered off. Then the aqueous layer is separated from the filtrate, and from it an additional amount of the copper complex is isolated by adding ethyl acetate. The precipitates are combined, washed with water, and dried at 100°. This gives 32 g of a greenish-colored substance. The substance is dissolved in dilute hydrochloric acid (1 : 2), the copper is precipitated with hydrogen sulfide, the copper sulfide is filtered off, charcoal is added to the filtrate, after which is evaporated with charcoal (to 1/2 of the volume); the charcoal is then filtered off and the mother liquor is neutralized with sodium carbonate to pH 3. During neutralization, a white amorphous precipitate forms, which is filtered off and washed with ice water (~75 ml).

It is dried at 120°. This gives 11 g of a white amorphous substance. Analysis for sodium shows its absence.

$C_6H_7O_3NPCl$.	Found, %:	P 15.02; 14.97; Cl 17.04; 17.02; N 7.01; 7.08
	Calculated, %:	P 14.92; Cl 17.06; N 6.75

An additional amount of chloro-*o*-aminobenzolphosphonic acid was isolated from the mother liquor in the form of an azo dye with resorcinol, in an amount of 7.3 g.

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* With the participation of G. B. Zavarikhina and G. P. Stepanova.

In the case of the *m*- and *p*-isomers, ethyl acetate is distilled off, copper is precipitated with hydrogen sulfide, the copper sulfide is filtered off, and the filtrate is boiled with charcoal until the odor of hydrogen sulfide is removed; it is then filtered and neutralized with sodium bicarbonate to pH ~3–4.

The resulting solution is diazotized and poured into an alkaline solution of resorcinol. The dye formed is isolated by acidification with hydrochloric acid and reprecipitated twice from water. It is dried at 70–80°. The weight of the substance obtained from the *m*-isomer is 11.8 g, and from the *p*-isomer 28.4 g. In both cases the dyes contain neither sodium nor chloride ion. As analyses showed, both are mixtures of two azo compounds, one of which (in a considerably smaller amount) contains chlorine in the molecule; it was not possible to separate them.

Substance from the *m*-isomer: Found, %: P 9.57; 9.67; Cl 2.1; 2.15

Substance from the *p*-isomer: Found, %: P 10.33; 10.48; Cl 2.4; 2.1

$C_{12}H_{11}O_5N_2P$. Calculated, %: P 10.57;
$C_{12}H_{10}O_5N_2PCl$. Calculated, %: P 9.40; Cl 10.78

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