solution of 1 ml (10 mmole) of phenylhydrazine in 5 ml of ethanol was added, and the mixture was refluxed for 5 h. It was then poured into water, and the precipitate was removed by filtration, washed with water, and dried.

The substances were purified by chromatography of benzene solutions of them on aluminum oxide.

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OXIDATION OF SOME HETARYLHYDRAZINES WITH SELENIUM DIOXIDE

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The oxidation of 2-benzimidazolyl- and 2-quinoxalinylhydrazines with selenium dioxide in hydrochloric acid in the presence of cuprous chloride leads to the formation of 2-chloro derivatives of the heterocycles. When the reaction is carried out in ethanol, 2-benzimidazolylhydrazines give symmetrical formazans. In both cases oxidation proceeds through a step involving the formation of hetarenediazonium salts.

The oxidation of aqueous acidic solutions of arylhydrazine with selenium dioxide leads to the formation of arylamines, azoamino derivatives, and, when azo components are present, azo dyes. It is assumed [1] that the reaction proceeds through the intermediate formation of arenediazonium derivatives.

It seemed of interest to study this reaction as applied to some heterocyclic hydrazines. With this as our goal, we investigated the oxidation of 2-benzimidazolyl- and 2-quinoxalinylhydrazines (Ia-c) with selenium dioxide. 2-Chloro-substituted derivatives (IIIa-c) were obtained in 37, 58, and 10% yields, respectively, by oxidation of these compounds in hydrochloric acid in the presence of cuprous chloride. The low yield of 2-chloroquinoxaline IIIc is due to its partial hydrolysis under the reaction conditions (or during its isolation) to 2-quinoxalone (IVc), which was isolated from the reaction mixture in 13% yield. The oxidation of phenylhydrazine under the same conditions gives chlorobenzene (IIId). The structures of all of the compounds were confirmed by comparison of their data and IR spectra with the data and spectra for genuine samples [2, 3].

$$\underset{\text{Ia-d}}{R{-}NH{-}NH_2} \xrightarrow[HCl]{SeO_2} \underset{\text{II}}{[R{-}N{\equiv}N]^+Cl^-} \xrightarrow[HCl]{Cu_2Cl_2} \underset{\text{IIIa-d}}{RCl} \xrightarrow{H_2O} \underset{\text{IVc}}{R{-}OH}$$

I, III, IV a R=2-benzimidazolyl, b R=1-methyl-2-benzimidazolyl, c R=2-quinoxalinyl, d $R=C_6H_5$

The formation of chloro derivatives can be explained if it is assumed that the oxidation of hydrazines I proceeds, as in the case of [1], through a step involving the formation of the corresponding diazonium salts II with subsequent replacement of the diazo group by chlorine in the presence of cuprous chloride. This reaction can be regarded as the variant of the Sandmeyer reaction as applied to nitrogen-containing heterocyclic compounds.

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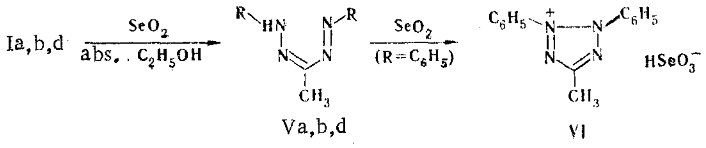
The oxidation of benzimidazolylhydrazines Ia, b with selenium dioxide in absolute ethanol proceeds via a different pathway. We found that in this case symmetrical 1,5-di(2'-benzimidazolyl)-3-methylformazans (Va, b) are formed in low (up to 18%) yields. Their structures were confirmed by comparison with compounds with known structures [4].



The formation of formazans V can be visualized if one assumes that the oxidation of hydrazines I in alcohol solution proceeds, just as in acidic solution, through the formation of a benzimidazolediazonium salt of the II type, which, inasmuch as it is extremely reactive [5], can oxidize ethanol to acetaldehyde. The excess hydrazine I can then react with the acetaldehyde to give the corresponding hydrazones, which undergo subsequent diazo coupling with the diazonium salt to give formazans V.

The proposed reaction scheme is confirmed by the experimental detection of acetaldehyde during the oxidation. The formation of acetaldehyde should be ascribed only to the reaction of the diazonium salt of the II type with alcohol, since it is known that selenium dioxide does not oxidize alcohol to acetaldehyde. The fact that formazan Vb is formed only in anhydrous alcohol also constitutes evidence in favor of this assumption. Virtually no reaction is observed in aqueous alcohol (40%). The direct oxidation of hydrazine Ib with SeO_2 in aqueous pyridine in the presence of a genuine sample of acetaldehyde 1-methyl-2-benzimidazolylhydrazone, which leads to symmetrical formazan Vb in 40% yield, serves as another confirmation of the proposed scheme for the formation of formazan Vb.

Phenylhydrazine (Id), like hydrazines Ia, b, also gives symmetrical 1,5-diphenyl-2-methylformazan (Vd), although in very low yield ($\sim$1%), when it is oxidized in absolute alcohol the process does not stop at this stage but proceeds further to give tetrazolium salt VI, which, without isolation from the solution, was reduced with ascorbic acid to formazan Vd by the method in [6]. The ease of oxidation of diarylformazans, particularly formazan Vd, to tetrazolium salts even by air oxygen was pointed out in [7, 8]. The structure of Vd was confirmed by comparison with a genuine sample [9].

Let us note that the oxidation of 2-hydrazinoquinoxaline Ic under the described conditions does not lead to the formation of formazans.

Thus the oxidation of heterocyclic hydrazines with selenium dioxide evidently proceeds, as in the case of arylhydrazines [1], through the formation of diazonium salts.

EXPERIMENTAL

Gas-liquid chromatography (GLC) was carried out with a Viruchrom chromatograph with a detector; the column was 2-m long with a diameter of 0.4 cm, the vaporized temperature was 200°C, the column temperature was 110°C, the detector temperature was 250°C, the stationary phase was DS-550, and the carrier gas was helium. The IR spectra were recorded with a UR-20 spectrometer.

Oxidation of 2-Hydrazino-1-methylbenzimidazole (Ib) in the Presence of Cu_2Cl_2. A 3-g (3 mmole) sample of cuprous chloride and 4.86 g (3 mmole) of Ib [2] were dissolved in 50 ml of concentrated HCl, after which a solution of 6.6 g (6 mmole) of selenium dioxide in 25 ml of water was added dropwise to the solution at 20-25°C. When vigorous nitrogen evolution was complete, the solution was heated to the boiling point, cooled, and filtered. The filtrate was neutralized to pH 5-6 with 30% NaOH solution, and the resulting precipitate was dried and extracted with alcohol. The solvent was removed by evaporation, and the dry residual 2-chloro-1-methylbenzimidazole (IIIb) was crystallized from water with the addition of activated charcoal to give 2.9 g (58%) of IIIb with mp 117-118°C (mp 117-118°C [10]).

Hydrazines Ia, c, d were oxidized under similar conditions, and the products were isolated by various methods.

Oxidation of 2-Hydrazinobenzimidazole (Ia). The resulting 2-chlorobenzimidazole (IIIa) was isolated in the same way as IIIb. The product was obtained in 37% yield and had mp 213-215°C (from 50% aqueous alcohol) (mp 212-215°C [11]).

Oxidation of 2-Hydrazinoquinoxaline (Ic). At the end of the reaction the precipitate was removed by filtration, dried, and extracted with chloroform. The solvent was removed by evaporation, and the residue was distilled *in vacuo* with collection of the fraction (10%) with bp 100-110°C [4-5 mm (mercury column)], which solidified to give a product with mp 46-48°C (mp 46-48°C [3]). The material that remained after extraction of chloroquinoxaline IIIc was treated with NaOH solution at 30-40°C, and the solution was filtered and neutralized with CH_3COOH. 2-Quinoxalone (IVc) was removed by filtration and crystallized from alcohol to give a product with mp 264-265°C (mp 265°C [3]) in 13% yield.

Oxidation of Phenylhydrazine (Id). The resulting chlorobenzene was removed from the reaction mixture by steam distillation and, after separation from the water and drying, was purified by distillation to give a product with bp 131°C and n_D^{20} 1.5246 (handbook data: bp 132°C and n_D^{20} 1.5248) in 19% yield.

Oxidation of Hydrazine Ib in Ethanol. A solution of 1.11 g (1 mmole) of selenium dioxide in alcohol was added dropwise at 10-15°C to a solution of 1.62 g (1 mmole) of Ib in 20 ml of absolute alcohol, and the mixture was allowed to stand at this temperature for 3-4 h. The precipitated selenium was removed by filtration, the filtrate was diluted with a fivefold volume of water, and the precipitated formazan Vb was crystallized from DMF–water (3:1) to give 0.6 g (18%) of Vb with mp 156-158°C (mp 156-158°C [4]).

Oxidation of 2-Hydrazinobenzimidazole (Ia). This reaction was carried out as in the preceding experiment, and the resulting 1,5-di(2'-benzimidazolyl)-3-methylformazan (Va) was crystallized from alcohol to give a product with mp 108-110°C (mp 110°C [4]) in 10.3% yield.

Oxidation of Phenylhydrazine in Alcohol. A solution of 19 g (17 mmole) of selenium dioxide in alcohol was added in the course of 30 min at –3 to 0°C to a solution of 24.5 g (22.6 mmole) of freshly distilled phenylhydrazine in 50 ml of absolute alcohol. The reaction proceeded with vigorous nitrogen evolution. After 1 h, the reaction mixture was evaporated, and the resinous residue was washed with benzene, dried, and extracted with water. The aqueous solution was made alkaline to pH 10 with 2 N NaOH solution, treated with charcoal, and filtered. The filtrate was diluted with 500 ml of water and 40 ml of alcohol, and an aqueous solution of ascorbic acid was added to it in small portions. The precipitated orange needles of 1,5-diphenyl-3-methylformazan (Vd) was removed by filtration, washed with water, and crystallized from 50% alcohol to give 0.3 g (1.3%) of Vd with mp 124-125°C (mp 125°C [9]).

Detection of Acetaldehyde. A solution of 1.62 g (1 mmole) of 2-hydrazino-1-methylbenzimidazole (Ib) in alcohol was added dropwise at 40-50°C to a solution of 1.11 g (1 mmole) of selenium dioxide in 30 ml of absolute alcohol, and the evolved gas (nitrogen and acetaldehyde) was bubbled through an aqueous solution of sodium nitroprusside and piperidine [12]. The dark-violet color of the reagent constituted evidence for the presence of acetaldehyde in the exhaust gas.

Oxidation of 2-Hydrazino-1-methylbenzimidazole (Ib) in the Presence of Acetaldehyde 1-Methyl-2-benzimidazolylhydrazone. A 5-ml sample of 30% NaOH was added to a solution of 0.9 g (5 mmole) of hydrazine Ib in 15 ml of pyridine, after which a solution of 0.7 g (6 mmole) of selenium dioxide in 10 ml of water was added dropwise at 10°C. After 1 h, the reaction mixture was filtered, and the filtrate was acidified to pH 4 with 10% hydrochloric acid. The precipitated formazan Ib was washed with water and crystallized from DMF–water (3:1) to give 0.7 g (40%) of symmetrical formazan Vb with mp 156-158°C (mp 156-158°C [4]).

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