INVESTIGATIONS OF BENZIMIDAZOLE DERIVATIVES

XXIV.* AZO COUPLING OF ARENES WITH BENZIMIDAZOLE-2-DIAZONIUM SALTS

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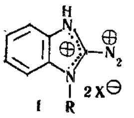
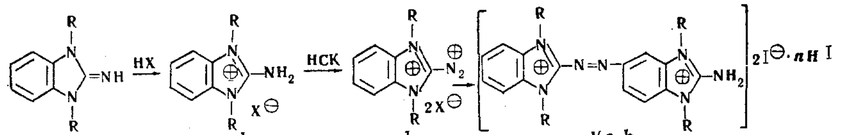
The high reactivity of benzimidazole-2-diazonium salts, which can couple with benzene and its homologs, is apparently due to the effect of a positively charged imidazole ring linked to the diazo group. The correctness of this assumption was proved by the formation of azo-compounds by the reaction of the 2-amino-1,3-dialkylbenzimidazolium salt, formed in an acidic medium from the corresponding imine, with nitrosylsulfuric acid ("self-coupling" reaction) or of the 2-amino-1,3,5,6-tetramethylbenzimidazolium salt with nitrosylsulfuric acid in the presence of toluene.

As was previously shown in [2], the simplest arenes readily couple with benzimidazole-2-diazonium salts (I), formed by the action of nitrosylsulfuric acid (XI) on 2-aminobenzimidazoles,† in concentrated sulfuric and phosphoric acids. Such high reactivity can be explained by the effect on the diazo group of the highly electrophilic, protonated imidazole ring linked to it [2, 4].



I

To verify the assumptions made, we introduced 2-imino-1,3-dialkylimidazolines II into the indicated transformations. In acidic media these compounds exist in the form of 2-amino-1,3-dialkylbenzimidazolium salts (III) [5], and, under the action of XI, should apparently be converted to diazonium salts IV, which contain a doubly charged cation. It might be expected that these salts will have the same properties as salts I.



IIa,b IIIa,b IVa,b Va,b

II–V a R = CH_3, n-2,5; b R = C_2H_5, n-1,5

In fact, reaction of 2-iminobenzimidazolines with XI in concentrated sulfuric and phosphoric acids gives azo compounds which, as in the case of 2-aminobenzimidazoles [3], are apparently formed by coupling of diazonium salt IV with the starting imine (II), which does not react with XI. The azo compounds are isolated (after pouring the reaction mixture into ice) in the form of iodides (V) that are only slightly soluble in water. As established in the case of Va, they are identical to the products of dialkylation of azo compounds VI, which are formed from 2-aminobenzimidazoles by "self-coupling." (See scheme, page 1460.)

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*See [1] for Communication XXIII.

† The 5 and 6 positions in these salts should be substituted; otherwise, "self-coupling" occurs [3].

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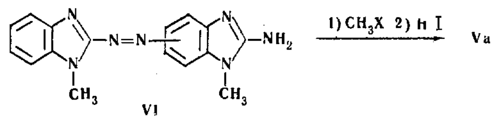
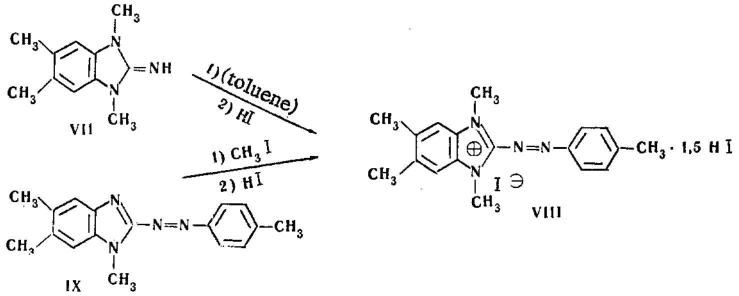


Compound II reacts considerably more slowly with XI than the corresponding 2-aminobenzimidazoles. Thus the process must be carried out for no less than 20 h to obtain a sufficiently high yield of Va and for 80-90 h to obtain sufficiently high yields of Vb. This is probably due to the steric effect of the alkyl radicals attached to the nitrogen atoms of the imidazole ring.

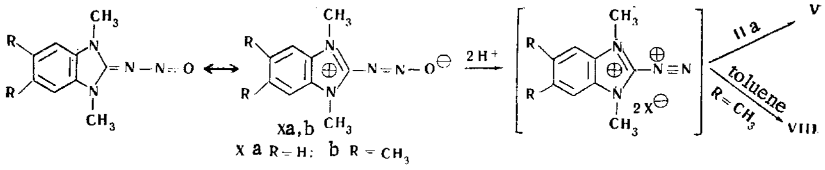
Dark-red V are stable iodide hydroiodides which decompose near their melting points. On prolonged treatment with water at 20° (faster with heating) they lose a portion of their ionogenic halogen and are converted to black substances with a metallic luster; these were not studied more closely.

If the 5 and 6 positions of II are substituted with, for example, methyl groups, as in VII, "self-coupling" becomes impossible since the 4 and 7 positions are inactive. The diazonium salts formed from VII will couple with azo components introduced into the reaction mixture, for example, arenes. However, in contrast to diazonium salts I, the diazo compound obtained from VII couples quite successfully only with toluene and only on prolonged reaction; traces of azo compounds, detected chromatographically, are formed with mesitylene, m-xylene, and benzene. In the first two cases, this may be due to a certain extent to both reaction of the arenes themselves with XI* and to steric hindrance arising during azo coupling. The chief reason, however, is the considerably lower activity of diazo compounds of the IV type as compared with that of I, as a result of which benzene, for example, undergoes virtually no coupling, and the yield of VIII from toluene is low (23%). Structure VIII was confirmed by alternative synthesis.

The heretofore unreported diazotization of imines apparently proceeds through N-nitroso compounds, in agreement with the concepts of the mechanism for the formation of diazonium salts [7]. In fact,



N-nitroso derivatives of 2-imino-1,3-dialkylbenzimidazolines [8], which exist as dipolar ions (inner diazotates) according to their IR spectra, form azo compounds that are identical to the previously described V or VIII when they are treated with concentrated H_2SO_4 in the presence of appropriate azo components.



The results confirm our assumptions regarding the structure and the reason for the high reactivity of benzimidazole-2-diazonium salts.

EXPERIMENTAL

Reaction of 2-Imino-1,3-dialkylbenzimidazolines (II) with XI. Compound IIa (0.01 mole) was dissolved in the cold in 15 ml of concentrated H_2SO_4, 2 g-equivalents of XI and 8-10 ml of concentrated H_3PO_4 were added to the ice-cooled solution, and the mixture was allowed to stand at room temperature for 30 h. The reaction with IIb was carried out similarly, but the reaction time was 90 h. The reaction mixture was

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*A mixture of substances, which is chromatographically similar to the mixture of compounds formed in azo coupling experiments (see [6]) is formed during prolonged (25-30 h) reaction of these arenes with XI.

poured over ice, urea was added to decompose the nitrous acid, and sufficient saturated potassium iodide solution to make the mother liquor above the precipitate almost colorless was added in the cold. The precipitate was washed with water and dried, first at 20° and then at 40-50°. The V obtained in this way were insoluble in water, quite soluble in acetone, and less soluble in alcohol (heating).

2-Amino-1,1',3,3'-tetramethyl-2',5-diazobenzimidazolium Diiodide (Va). A. Compound Va was obtained in 66% yield by reaction of IIa with XI. Dark-red needles with mp 253-254° (from acetone with water) Found %: I 63.04; N 10.86. $C_{18}H_{21}I_2N_7 \cdot 2.5HI$. Calculated %: I 62.82; N 10.79.

B. N-Nitroso-2-imino-1,3-dimethylbenzimidazole (Xa) [8] was dissolved in the cold in a mixture of concentrated H_2SO_4 and H_3PO_4, an equivalent amount of IIa was added, and the mixture was allowed to stand for 25-30 h. It was then poured over ice and treated as described above to give 30% of Va.

C. A mixture of isomeric azo compounds (VI) [3] was heated with 4 mole of freshly distilled methyl benzenesulfonate at 100°. After 1 h, the melt was cooled and triturated with ether. The residue was dissolved in water, and the solution was saturated with potassium iodide. The precipitate is the diiodide of the azo compound, which differs from Va in the absence of hydriodic acid in the crystals and the different character of the UV-absorption spectrum. The yield of the brick-red needles with mp 254-255° (from acetonitrile with acetone) was 78%. Found %: I 43.54. $C_{18}H_{21}I_2N_7$. Calculated %: I 43.08. After treatment in the cold with dilute hydriodic acid and drying at 40-50°, the compound was identical to the samples obtained via methods A and B.

2-Amino-1,1',3,3'-tetraethyl-2',5-diazobenzimidazolium Diiodide (Vb). This was obtained in 52% yield from IIb. Dark-red needles with mp 245° (from aqueous alcohol). Found %: I 53.60; N 11.98. $C_{22}H_{29}I_2N_7 \cdot 1.5HI$. Calculated %: I 53.05; N 11.71.

1,3,5,6-Tetramethyl-2-iminobenzimidazoline (VII). This was obtained by alkylation [9] of 2-amino-1,5,6-trimethylbenzimidazole [10] in alcoholic methyl iodide (2 mole) with subsequent treatment with alkali. Yield 85%. Snow-white needles with mp 156° (from aqueous alcohol). Found %: C 69.61; H 7.87; N 22.27. $C_{11}H_{15}N_3$. Calculated %: C 69.81; H 7.99; N 22.20.

2-(p-Tolyldiazo)-1,5,6-trimethylbenzimidazole (IX). This was obtained in 63% yield by reaction of 1,5,6-trimethyl-2-aminobenzimidazole with XI and toluene by the method described in [2]. Light-orange plates (from hexane) with mp 198°. Found %: C 73.10; H 6.68. $C_{17}H_{18}N_4$. Calculated %: C 73.35; H 6.52.

2-Nitrosimino-1,3,5,6-Tetramethylbenzimidazoline (Xb). This was obtained in 92% yield via the method in [8] at 60-70°. Light-yellow needles which decompose explosively at 150° (from alcohol or acetone. Found %: N 25.42. $C_{11}H_{14}N_4O$. Calculated %: N 25.67.

2-(4'-Tolyldiazo)-1,3,5,6-tetramethylbenzimidazolium Iodide (VIII). A. Compound VII [0.95 g (5 mmole)] was dissolved in the cold in a mixture of 10 ml of concentrated H_2SO_4 and 5 ml of concentrated H_3PO_4, 1 ml of toluene and 10 mmole of XI were added, and the mixture was shaken at 20-25° for 30-35 h. The mixture was then poured over ice, and a saturated solution of potassium iodide was added. The precipitate was washed with water, dried at 50°, and treated with boiling acetone (three to four times with 50-ml portions). The residue contained iodide which had not reacted with VII (41%). The acetone extract was evaporated, and the residue was washed with ether and a small amount of alcohol to give 23% of dark-cherry prisms with mp 231-232° (from acetone or chloroform) and λ_{max} 404-410 nm and log ε 4.38 (methanol). Found %: I 52.02; N 9.58. $C_{18}H_{21}IN_4 \cdot 1.5HI$. Calculated %: I 51.82; N 9.15.

B. N-Nitroso-2-imino-1,3,5,6-tetramethylbenzimidazoline and a twofold excess of toluene were shaken with concentrated H_2SO_4 for 30-35 h. Compound VIII (27%) was isolated as described in A.

C. Compound IX was alkylated in alcoholic methyl iodide (2 mole) for 3-4 h to give 94% of dark-cherry prisms of a product with mp 231-232° (from alcohol), which differed from VIII obtained by methods A and B in that it did not contain hydriodic acid and had a different UV-absorption spectrum. Found %: I 30.54; N 13.48. $C_{18}H_{21}IN_4$. Calculated %: I 30.19; N 13.33. Treatment of the compound obtained with dilute hydriodic acid gave a compound that was identical to that obtained via methods A and B.

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