

BENZ- AND NAPHTHAZOLE RESEARCH. XI. * FORMAZANES
OF THE NAPHTH[1, 2-d]IMIDAZOLE SERIES

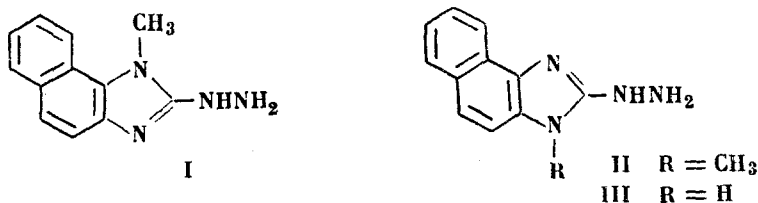
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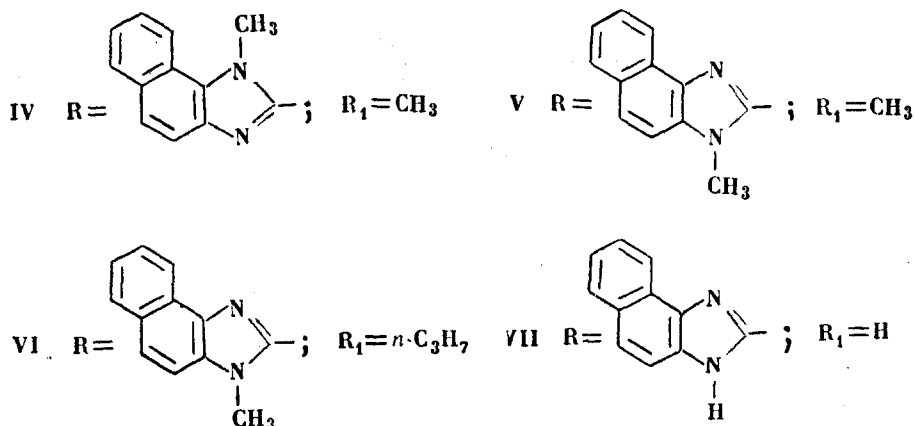
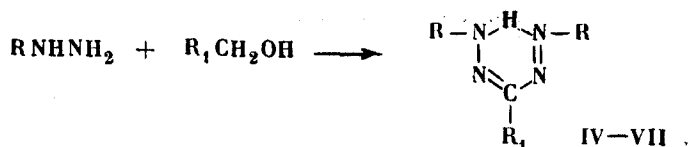
Like 1-alkyl-2-hydrazinobenzimidazoles, 2-hydrazinonaphth[1, 2-d]imidazole and 1-methyl- or 3-methyl-2-hydrazinonaphth[1, 2-d]imidazoles, when dissolved in dry alcohols, undergo autoxidation to 1, 5-dinaphth[1, 2-d]imidazolyformazanes.

It was previously shown [2] that 1-alkyl-2-hydrazinobenzimidazoles, dissolved in alcohols, undergo autoxidation with the oxygen of the air to give 1, 5-dibenzimidazolyformazanes, dark violet crystalline substances. The aim of the present work was to explore the possibility of obtaining formazanes of the naphth[1, 2-d]imidazole series in a similar way.

Research with the solutions previously described [3], viz., 1-methyl-2-hydrazinonaphth[1, 2-d]imidazole (I), 3-methyl-2-hydrazinonaphth[1, 2-d]imidazole (II), and 2-hydrazinonaphth[1, 2-d]imidazole (III) in dry alcohols (CH₃OH,



C₂H₅OH, n-C₄H₉OH), showed that they, like 1-alkyl-2-hydrazinobenzimidazoles, suffer autoxidation in the course of several days, being changed into the corresponding 1, 5-dinaphth[1, 2-d]imidazolyformazanes.



1, 5-dinaphth[1, 2-d]imidazolyformazane (VII) is obtained by autoxidation of the hydrazine, but also from hydrazine II and orthoformic ester.

Naphthimidazole formazanes are much more deeply colored (almost black) than 1, 5-dibenzimidazolyformazanes, the absorption curve maxima being considerably displaced towards the long wavelength region (570 mμ instead of 520-530 mμ). Unlike other formazanes of benz- and naphthimidazole, formazanes V and VI have an inflection directed towards the short wavelength part of the spectrum (see Table), in addition to the main absorption band. 1, 5-dinaphth[1, 2-d]imidazolyformazanes are less soluble in organic solvents than 1, 5-dibenzimidazolyformazanes. All the formazanes prepared have firmly held water of crystallization as part of the molecule, though they lose it when vacuum-dried at the temperature of boiling xylene, undergoing partial reconversion on standing in air. Naphthimidazole formazanes react with copper salts to give complexes that are almost black microcrystalline powders, melting above 350°.

*For part X see [1].

EXPERIMENTAL

Formazanes IV and V. A saturated alcohol solution of the hydrazino derivative (4.3 g hydrazine I in 150 ml or 4.3 g hydrazine II in 300 ml alcohol) is allowed to stand in a flask plugged with cotton wool. Initially, the solution is yellow, then it becomes green, next blue, and finally dark violet. In a week, crystals separate. In bulk, formazane IV is black with a green reflex. Yield 11-14%. Formazane V is dark brown, with a green reflex. Yield 40-42%.

Formazane VI is prepared similarly, by allowing a solution of the hydrazine II in n-butanol to stand. Dark green crystals with a yellow reflex. Yield about 20%.

Formazane VII

a) A solution of 1 g hydrazine III in 200 ml 95% methanol containing 1 ml pyridine autoxidizes slowly, after a fortnight dark green crystals appear. Yield 26%.

b) A mixture of 1 g hydrazine III in 10 ml orthoformic ester plus 2.5 ml water is heated for 1 hr on a water bath, and the viscous violet solution left overnight. The crystals which separate resemble those of a). Yield 17%.

c) Formazanes dissolve on heating in dioxane, dichloroethane, chloroform (reddish-violet solutions), dissolve readily in dimethylformamide (bluish-violet solutions), and have low solubilities in acetone, alcohol, and benzene, while they are insoluble in water and dilute acids. The formazane VII is readily soluble in dilute alkalies giving blue solutions.

The spectra were observed with an SF-2M spectrophotometer, the solvent being chloroform, solution concentration 10^{-4} mole/l, layer thickness 3.05 mm.

REFERENCES

1. Yu. A. Rybakova and N. P. Bednyagina, ZhOKh, Collection 2, 1965.
2. N. P. Bednyagina, G. N. Tyurenkova, Yu. A. Rybakova, ZhOKh, 34, 1288, 1964.
3. N. P. Bednyagina, I. N. Getsova, and I. Ya. Postovskii, ZhOKh, 32, 3015, 1962.

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1, 5-Dinaphth[1, 2-d]imidazolylformazanes

Compound	Name ^e	Mp, °C	Spectral characteristics $\lambda_{max}, m\mu$ (log ϵ)	Formula	Found, %				Calc., %			
					C	H	N	H ₂ O	C	H	N	H ₂ O
IV	1, 5-Di(1'-methylnaphth[1, 2-d]imidazolyl-2')-3-methylformazane	191-193 (decomp.)	568 (4.71)	$C_{26}H_{22}N_8 \cdot 2H_2O$	64.88	5.42	22.92	7.64	64.71	5.43	23.20	7.46
V	1, 5-Di(3'-methylnaphth[1, 2-d]imidazolyl-2')-3-methylformazane	169-172 (decomp.)	552 (4.64); 570 (4.65)	$C_{26}H_{22}N_8 \cdot 2\frac{1}{2}H_2O$	62.99	5.91	22.20	9.45	63.52	5.53	22.79	9.16
VI	1, 5-Di(3'-methylnaphth[1, 2-d]imidazolyl-2')-3-propylformazane	172-174 (decomp.)	552 (4.68); 576 (4.69)	$C_{28}H_{26}N_8 \cdot 1\frac{1}{2}H_2O$	67.10	5.87	21.55	5.58	67.04	5.83	22.34	5.35
VII	1, 5-Di(naphth[1, 2-d]imidazolyl-2')-formazane	214-217 (decomp.)	536 (4.26)	$C_{23}H_{16}N_8 \cdot 2H_2O$	62.08	4.37	24.88	7.38	62.71	4.57	25.44	8.18