UDC 547.78 + 542.959 + 543.422

STUDIES IN THE BENZAZOLE AND NAPHTHAZOLE SERIES. VIII*. REACTION OF 2-HYDRAZINONAPHTH[1, 2-d]IMIDAZOLE AND ITS 1- AND 3-METHYL DERIVATIVES WITH CARBON DISULFIDE

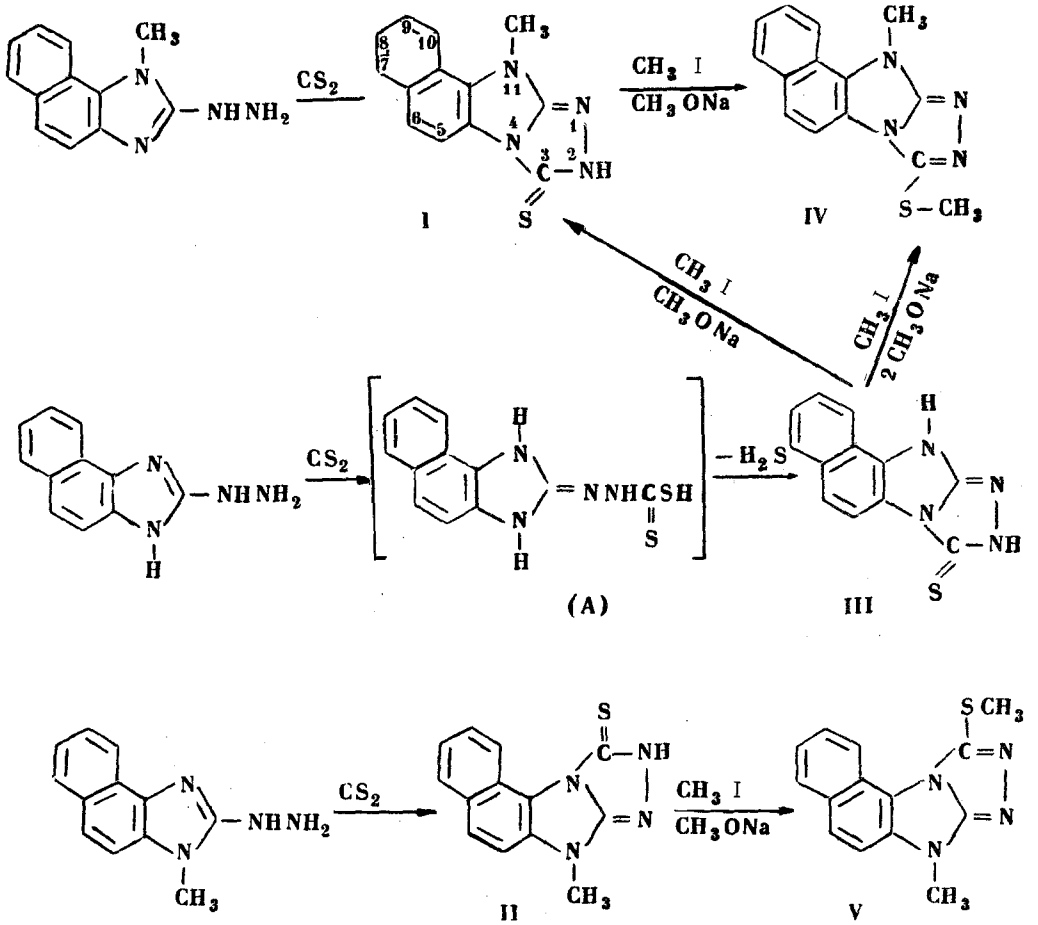
I. N. Getsova, L. L. Sribnaya, N. P. Bednyagina

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, pp. 129-132, 1965

When heated with carbon disulfide in pyridine 2-hydrazinonaphth[1, 2-d]imidazole yields S-triazolo[4, 3-b]-naphth[1, 2-d]imidazole-3-thione. Kinetic and not steric factors determine the formation of this compound. Its trans-angular structure is demonstrated by the agreement between its UV spectrum and that of 11-methyl-S-triazolo[4, 3-b]naphth[1, 2-d]imidazole-3-thione, prepared from 1-methyl-2-hydrazinonaphth[1, 2-d]-imidazole and carbon disulfide, as well as by the identity of their methylation products. Methyl iodide methylation, in the presence of sodium methoxide, of S-triazolo[4, 3-b]naphth[1, 2-d]imidazole-3-thione, like that of S-triazolo[4, 3-a]benzimidazole-3-thione, takes place stepwise. First the methyl group adds to the nitrogen atom of the imidazole ring, and only then to the thiol group of the triazole ring.

When 2-hydrazinobenzimidazole reacts with carbon disulfide, it forms S-triazolo[4, 3-a]benzimidazole-3-thione [1, 2]. 2-Hydrazinonaphth[1, 2-d]imidazole and its 1- and 3-methyl-substituted derivatives react similarly with carbon disulfide. Heating in pyridine leads to evolution of hydrogen sulfide and precipitation of crystals of S-triazolonaphth-[1, 2-d]imidazole-3-thiones.

In this reaction 1-methyl-2-hydrazinonaphth[1, 2-d]imidazole gives 11-methyl-S-triazolo[4, 3-b]naphth[1, 2-d]-imidazole-3-thione (I) with the rings trans-angular (see equations), and 3-methyl-2-hydrazinonaphth[1, 2-d]imidazole forms the isomeric 11-methyl-S-triazolo[4, 3-a]naphth[1, 2-d]imidazole-3-thione (II), with a cis-angular structure. Both reactions take place under identical conditions and give identical yields of products. Evidently steric hindrance, which could come from the direction of the α positon in the naphthalene ring, does not affect the course of the reaction by which the cis-angular isomer II is formed.

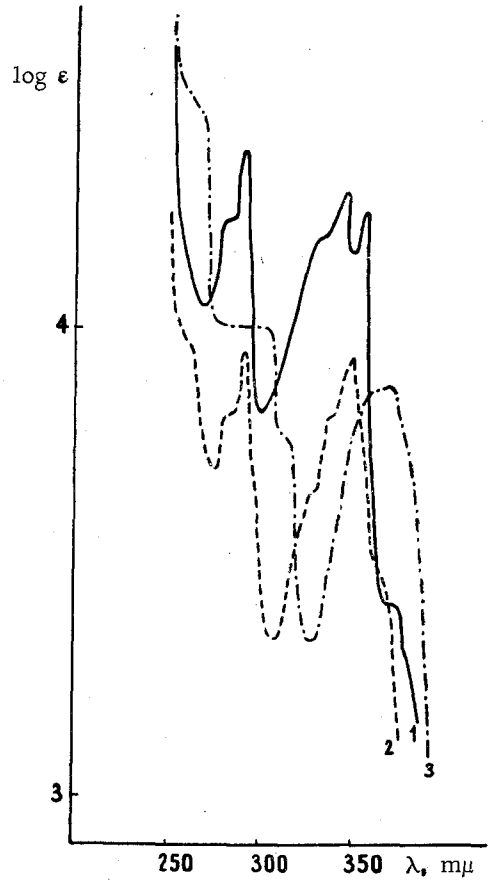


*For Part VII see [3].

Reaction of carbon disulfide with 2-hydrazinonaphth[1, 2-d]imidazole, with an unsubstituted nitrogen atom, can give a mixture of cis- and trans-angular isomers with one of them predominating, due to the asymmetry of the molecule and the inequality of the nitrogen atoms of the imidazole ring. However, in a reaction giving a 93-95% yield only one compound was obtained, so that reaction proceeds mainly with formation of one isomer. To elucidate the structure of III, the UV spectra of compounds I, II, and III were determined. It can be seen from the figure that the absorption curve for III repeats that for compound I, which has a trans-angular structure. On the other hand, the UV spectrum of the cis-angular compound II differs from the spectra of the other two compounds. Hence it can be concluded from the UV spectra that compound III has a trans-angular structure.

Comparison of the methylation products derived from I, II, and III leads to the same conclusion. These compounds can be methylated only in the presence of the calculated amount of alkali or sodium methoxide (heating with excess of alkali makes the reaction mixture turn blue and there is a marked smell of methyl mercaptan). Action of excess methyl iodide in methanol in the cold on III, using sodium methoxide in the proportion of 1 gram-atom of sodium to 1 mole compound, gives a 70% yield of crystalline methylation product identical with compound I and known to have a trans-angular structure. Methylation of compound III, using 2 moles sodium methoxide led to isolation of a product identical with compound IV, also obtained by methylating compound I.

It is of interest to note that methylation of III in a molar solution of sodium methoxide proceeds stepwise, and obviously the rate of methylation at the imidazole ring nitrogen atom is considerably greater than that at the triazolethione sulfur atom. The existence of stepwise methylation was verified for S-triazolo[4, 3-a]benzimidazole-3-thione, and the same relationship was found. The action in the cold of the calculated quantity of sodium methoxide and excess methyl iodide leads first to methylation in the imidazole ring and formation of 9-methyl-S-triazolo[4, 3-a]benzimidazole-3-thione. On subsequent methylation using excess alkali we get methylation at the thiol group to give 9-methyl-S-triazolo-[4, 3-a]benzimidazole-3-methylthiol [3].



UV spectra in dimethylformamide: 1. S-Triazolo[4, 3-b]naphth[1, 2-d]imidazole-3-thione (III); 2. 11-Methyl-S-triazolo[4, 3-b]-naphth[1, 2-d]imidazole-3-thione (I); 3. 11-Methyl-S-triazolo[4, 3-a]naphth[1, 2-d]imidazole-3-thione (II).

In the case of the reaction of 2-hydrazinonaphth[1, 2-d]imidazole with carbon disulfide, position 3 in the naphthimidazole ring is more reactive than position 1 for hydrogen substitution in polar media. Preferential reaction at position 3 in alkylation of 2-chloronaphth[1, 2-d]imidazole with alkyl halides in alcoholic alkali has already been noted [4]. Probably in this particular case the unstable intermediate product arising through addition of carbon disulfide to 2-hydrazinonaphth[1, 2-d]imidazole (A) very rapidly splits off hydrogen sulfide, which is derived from the SH group and the hydrogen in position 3 (but not 1) of the naphthimidazole ring, so that the yield of the final product is determined by kinetic and not steric factors.

EXPERIMENTAL

S-Triazolo[4, 3-b]naphth[1, 2-d]imidazole-3-thione (III). 7 ml carbon disulfide is added to 8.8 g 2-hydrazinonaphth[1, 2-d]-imidazole dissolved in 40 ml pyridine, the mixture is refluxed for 8 hr and diluted with water. The precipitate is filtered off, and washed well with water, yield 10.0 g. It is then dissolved in very dilute NaOH solution, treated with charcoal, and precipitated with acid. Flat elongated hexagons (from dimethylformamide) or fine needles (from dimethylformamide-alcohol) are formed. Yields a crystalline sodium salt (with an alcoholic solution of sodium ethoxide), and is readily hydrolyzed on dissolving in water. Compounds I and II are prepared in the same way, heating time 4 hr. The table gives the constants of the substances.

Methylation of compound III to I. A solution of sodium methoxide prepared from 0.12 g (0.005 gram-atom) Na and 25 ml methanol is added to 1.2 g (0.005 mole) III in 10 ml anhydrous methanol, and the mixture left at room temperature for a few hours. The precipitate formed is filtered off, m.p. 260-262°, mixed m.p. with I, prepared above, undepressed.

Methylation of compound III to IV. A solution of sodium methoxide, prepared from 0.23 g Na (0.01 gram-atom) and 40 ml methanol is added to 1.2 g (0.005 mole) III suspended in 5 ml methanol, followed by 1 ml methyl iodide. The dark solution is left overnight, and then evaporated to dryness. The colorless residue is carefully washed with water, yield 1 g. I and II were methylated in the same way as III to I.

9-Methyl-S-triazolo[4, 3-a]benzimidazole-3-thione. A solution of sodium methoxide prepared from 0.12 g Na (0.005 gram-atom) in 20 ml methanol was added to 0.95 g (0.005 ml) S-triazolo[4, 3-a]benzimidazole-3-thione, suspended in 5 ml methanol, followed by 0.5 ml methyl iodide. Fine clusters of needles begin to be precipitated abruptly; and after some minutes the solution is filled with a compact mass of crystals. Yield 70-80%. After three crystallizations from alcohol it melts at 260-265°, undepressed on admixture of product from 1-methyl-2-hydrazinobenzimidazole and carbon disulfide [3].

Melting points, yields, and analytical data for compounds synthesized

Compound	M.p., °C	Crystallization solvent	Empirical formula	Found, %		Calculated, %		Yield, %
				N	S	N	S	
I	262—264	Dimethyl +alcohol	$C_{13}H_{10}N_4S$	21.72	12.00			80 (from III), 70
II	237—238	Dimethyl +alcohol	$C_{13}H_{10}N_4S$	22.20	12.12	22.03	12.60	85
III	Above 360	As in II	$C_{12}H_8N_4S$	23.99	13.48	23.32	13.34	93—95
IV	183—184	Alcohol	$C_{14}H_{12}N_4S$	20.58	11.73	20.81	11.95	80 (from I), 77 (from III)
V	195—196	Alcohol	$C_{14}H_{12}N_4S$	20.68	11.90			80 (from II)

REFERENCES

1. Kodak Soc. Anon., Belg. Pat. 559022 (1957); C. A., 54, 132, 1960.

2. N. P. Bednyagina, I. Ya. Postovskii, Summary, VIII Mendeleev Conference, Org. Chem. Section, 331, AN SSSR, 1959.

3. N. P. Bednyagina, I. I. Getsova, ZhOrKh, no. 1, 1965.

4. N. P. Bednyagina, I. N. Getsova, and I. Ya. Postovskii, ZhOKh, 32, 3011, 1962.

7 October 1963

Kirov Urals Polytechnic Institute, Sverdlovsk