BENZAZOLES AND NAPHTHAZOLES. XXVII†. THE SYNTHESIS OF NAPHTH[1, 2-d]THIAZOLE FORMAZANS

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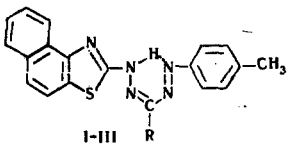
Coupling p-tolyldiazonium salts with hydrazones of 2-hydrazinonaphth-[1,2-d]thiazole gives the unsymmetrical 1-napth[1, 2-d]thiazolyl-3-aryl(or methyl)-5-p-tolylformazans. Conclusions concerning their structure are drawn on the basis of the IR and UV spectral data, and comparisons are made with the isomeric naphth[2, 1-d]thiazole formazans.

In continuation of investigations into relationship between color and structure in heterocyclic formazans, we have synthesized for the first time unsymmetrical naphth[1, 2-d]thiazole formazans, I-III.



I-III R

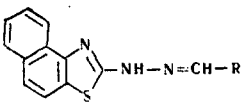
I R = CH_3;
II R = C_6H_5;
III R = p-$C_6H_4NO_2$

The starting 2-hydrazinonaphth[1, 2-d]thiazoles was obtained previously [1] from 4-α-naphthylthiosemicarbazide by oxidation with bromine in chloroform. The hydrazones were obtained in the usual way by heating equimolecular amounts of hydrazine and the appropriate aldehyde in alcohol. The properties and analytical data for the hydrazones are given in Table 1.

The unsymmetrical formazans I-III were obtained by coupling p-tolyldiazonium chloride with the appropriate hydrazone in alcoholic alkali, in a similar way to the synthesis of naphth[2, 1-d]thiazole formazans [2]. They are crystalline, high-melting, colored compounds, which are soluble in the usual solvents (appreciably more so than the isomeric naphth[2, 1-d]thiazole formazans). Properties and analytical data for these formazans are given in Table 2.

† For Part XXVI, see [4].

TABLE 1



R	Mp, °C	Appearance	Molecular formula	Found, %		Calculated, %		Yield, %
				N	S	N	S	
CH_3	178—179	Colorless needles (aqueous alcohol)	$C_{13}H_{11}N_3S$	16,83	12,97	17,41	13,28	75
C_6H_5	195—196	Colorless prisms (methanol)	$C_{18}H_{13}N_3S$	14,20	10,61	13,85	10,57	57
p-$C_6H_4NO_2$	266—267	Brick-red prisms (isopropanol)	$C_{18}H_{12}N_4O_2S$	16,02	8,53	15,64	8,91	

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TABLE 2. Properties of Naphth[1, 2-d]thiazole and Naphth[2, 1-d]thiazole Formazans

Compound	R	Mp, °C	IR spectrum ν_{NH} (3400-3100 cm^{-1})*	UV spectrum*, λ_{max}, nm, alcohol			Molecular formula	Found, %				Calculated, %				Yield, %
				pH 7	HCl, pH 1—2	NaOH, pH 10—12		C	H	N	S	C	H	N	S	
I	CH_3	101—103** Alcohol	3343 (3520)	420 (440)	414 (412)	566 (546)	$C_{20}H_{17}N_5S \cdot 1/2H_2O$**	64,89	4,93	18,97	8,53	65,21	4,89	19,02	8,69	80
II	C_6H_5	186—187 Aqueous dioxan	None („)	494 (492)	430 (480)	560 (550)	$C_{25}H_{19}N_5S$	71,41	4,57	16,24	—	71,23	4,56	16,61	—	90
III	p-$C_6H_4NO_2$	222—223 Alcohol-benzene	None („)	504 (496)	434 (494)	560 (558)	$C_{25}H_{18}N_6O_2S \cdot 1/2C_6H_5$***	66,69	4,38	16,73	6,46	66,51	4,18	16,62	6,43	83

* Results for naphth[2, 1-d]thiazole formazans are given in parentheses.

** After drying in vacuo over P_2O_5, mp 178-179° (decomp.). Found: H_2O 2.16%. $C_{20}H_{17}N_5S \cdot 1/2H_2O$. Calculated: H_2O 2.44%.

*** Loss in weight on drying 8.33%. $C_{25}H_{18}N_6O_2S \cdot 1/2C_6H_5$. Calculated %: C_6H_5 7.72.

Comparison of the spectra of I-III with those of the isomeric naphth[2, 1-d]thiazole formazans [2] in the visible and infrared regions suggests that the structure of the naphthothiazole ring has little or no influence on the structure of the formazan ring (Hausser et al. have made a similar observation in the case of the α- and β-naphthylformazans [3]).

LITERATURE CITED

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