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RESEARCH ON BENZO- AND NAPHTHAZOLES

XIII. Synthesizing Unsymmetrical Formazans of the Benzoimidazole Series*

Yu. A. Rybakova and N. P. Bednyagina

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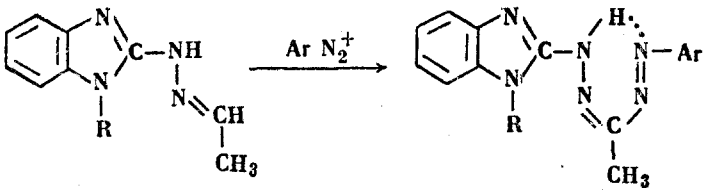
Fourteen unsymmetrical 1-(1'-alkylbenzoimidazolyl-2')-3-methyl-5-arylformazans are synthesized by nitrogen coupling of aryl diazonium salts with acetaldehyde 1-alkylbenzoimidazolyl-2-hydrazones, and their visible absorption maxima are given.

Tetrazenes are the usual intermediates formed by reaction of aryldiazonium salts with hydrazones prepared from primary aromatic hydrazines and aldehydes, and in alkali or on heating they rearrange to 1,5-diarylformazans [1, 2].

The present paper describes the synthesis of 1-(1'-alkylbenzoimidazolyl-2')-3-methyl-5-arylformazans, effected by nitrogen coupling of various diazonium salts with acetaldehyde N-alkylbenzoimidazolylhydrazones



R = $CH_2C_6H_5$; CH_3; Ar = *p*-$C_6H_4CH_3$; *p*-C_6H_4Cl; *o*-, *m*- or *p*-$C_6H_4NO_2$; $C_6H_2(NO_2)_2OH$; *o*-C_6H_4OH; *o*-C_6H_4COOH; *p*-C_6H_4—C_6H_4-*p*.

A solution of the aryl diazonium chloride was mixed with an alcoholic solution of the hydrazone, the mixture brought to pH 5-6 with 2 N NaOH solution, and diluted with water, when crystals precipitated. Recrystallization from alcohol, or alcohol-chloroform gave coarsely crystalline materials, whose color depended on the nature of the diazo- component, and ranged from orange to violet, with a metallic glance of various shades. These substances were 1-(1'-alkylbenzoimidazolyl-2')-3-methyl-5-arylformazans (see table).

In no case did it prove possible to detect formation of the possible intermediates, the tetrazene (a product of coupling at the alpha nitrogen of the hydrazone) or the diazoamino compound (a product of coupling at the nitrogen at the 3-position in the imidazole ring).

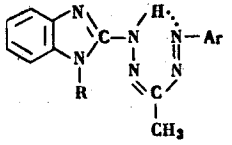
To a considerable extent the unsymmetrical formazans prepared share the properties of arylformazans, and of the previously described [3] 1,5-dibenzoimidazolylformazans. They are compounds which are stable in solution and in the crystalline state. Most melt with decomposition, but some (I, XI, XII) do not decompose, and on recrystallizing, they melt from alcohol, and the initial formazan is recovered with the same melting point. Like 1,5-dibenzoimidazolylformazans, many of the 1-benzoimidazoyl-5-arylformazans contain a component (water, alcohol) of crystallization.

The formazans prepared have rather good solubilities in organic solvents, giving solutions with beautiful rich tones, and are insoluble in water. They are amphoteric, and function as indicators. When solutions of them in water-miscible solvents are rendered alkaline, the color deepens markedly. Thus with formazans I-IV, alcohol solutions change in color, on making alkaline, from yellowish brown to reddish violet, with V-VIII from red to violet, and with formazans IX-XI and XIII, XIV, containing nitro- groups, from reddish-violet to deep blue. Like the arylformazans [4], they are stable even when heated in alkaline solution, but readily decomposed by acids. They are less stable to acids than the symmetrical 1,5-dibenzoimidazolylformazans. Formazanes with nitro- and carboxyl groups dissolve in concentrated sulfuric acid to give a blue color, those with methyl and halogen give a violet color, and those with an ortho-hydroxyl group give a green color. After a few minutes the color disappears.

The visible absorption spectra of these formazans enable conclusions to be drawn regarding the effect of substituents in the imidazole portion and 5-aryl one on formazan color. A substituent (benzyl or methyl) at the nitrogen of the benzimidazole ring is completely without effect on the position of the visible maximum. Formazans with the electron-donating groups CH_3, Cl, OH (I-VI) in the aryl portion are much more highly colored than those containing electron-accepting groups. A nitro- group in the ortho- (XI) or meta-position (XII) causes little displacement of the maximum, but in the para-position the nitro group (IX) has a considerable bathochromic effect.

*For Part XII see [6].

1-(1'-Alkylbenzoimidazolyl-2')-3-methyl-5-arylformazans.



Compound no.	R	Ar	Mp, °C	Color and crystal shape	λ_{max}, mμ	ε · 10^{-4}	Formula	Found, %		Calculated, %		Yield, %
								N	C, H, Cl	N	C, H, Cl	
I	$CH_2C_6H_5$	*p*-$C_6H_4CH_3$	121—124	Glistening orange-brown needles	452	3.47	$C_{23}H_{22}N_6 \cdot C_2H_5OH$	20.01	C 69.57 H 6.32	19.61	C 70.07 H 6.58	57
II	CH_3	*p*-$C_6H_4CH_3$	193—194	Orange plates	452	4.03	$C_{17}H_{18}N_6$	27.15	—	27.42	—	70
III	$CH_2C_6H_5$	*p*-C_6H_4Cl	187—188	Reddish-orange needles with a bluish reflex	468	4.19	$C_{22}H_{19}N_6Cl \cdot 2H_2O$	18.87	Cl 8.02	19.14	Cl 8.07	65
IV	CH_3	*p*-C_6H_4Cl	150—154	Orange-red plates	468	3.80	$C_{16}H_{15}N_6Cl \cdot H_2O$	24.40	Cl 10.50	24.38	Cl 10.28	70
V	$CH_2C_6H_5$	*o*-C_6H_4OH	189—190	Brown needles with a yellow reflex	486	3.67	$C_{22}H_{20}N_6O \cdot H_2O$	20.35	C 65.89 H 5.74	20.88	C 65.65 H 5.58	65
VI	CH_3	*o*-C_6H_4OH	202—203	Brown needles with a yellow reflex	486	3.67	$C_{16}H_{16}N_6O \cdot H_2O$	26.01	—	25.75	—	72
VII	$CH_2C_6H_5$	*o*-C_6H_4COOH	148—150	Red plates with a green reflex	530	5.57	$C_{23}H_{20}N_6O_2 \cdot H_2O$	19.21	C 63.92 H 5.36	19.52	C 64.10 H 5.15	64
VIII	CH_3	*o*-C_6H_4COOH	192	Small clusters of red needles	530	5.40	$C_{17}H_{16}N_6O_2 \cdot C_2H_5OH$	21.78	C 59.08 H 5.50	21.92	C 59.67 H 5.79	73
IX	$CH_2C_6H_5$	*p*-$C_6H_4NO_2$	238—239	Glistening blackish-blue needles	522	3.96	$C_{22}H_{19}N_7O_2$	23.81	C 63.42 H 4.51	23.71	C 63.99 H 4.87	66
X	CH_3	*p*-$C_6H_4NO_2$	226—228	Violet rhombs with a green reflex	522	4.16	$C_{16}H_{15}N_7O_2$	29.23	—	29.07	—	63
XI	$CH_2C_6H_5$	*o*-$C_6H_4NO_2$	105—108	Clusters of brown needles	486	3.63	$C_{22}H_{19}N_7O_2$	24.04	—	23.71	—	50
XII	$CH_2C_6H_5$	*m*-$C_6H_4NO_2$	106—110	Pale red needles	482	3.96	$C_{22}H_{19}N_7O_2 \cdot H_2O$	22.51	—	22.72	—	68
XIII	$CH_2C_6H_5$	$C_6H_2(NO_2)_2OH$	201—202	Dark violet rhombs with a golden reflex	545 650	3.96 2.67	$C_{22}H_{18}N_8O_5$	24.16	C 55.28 H 3.88	23.62	C 55.69 H 3.82	87
XIV	$CH_2C_6H_5$	$(p\text{-}C_6H_4)_2$	245	Glistening reddish black plates	508	8.24	$C_{44}H_{38}N_{12}$	22.39	C 72.01 H 5.32	22.87	C 71.91 H 5.21	95

Experimental

Acetaldehyde 1-benzylbenzoimidazolyl-2-hydrazone. 7 g 1-benzyl-2-hydrazinobenzoimidazole [5] was mixed with 10 ml acetaldehyde, and when the first vigorous reaction had ended, the mixture was refluxed for 30 min on a steam bath, and the precipitate filtered off and washed with ether. Yield 7 g (90%), mp 138-139°, readily soluble in most organic solvents. Hydrochloride mp 213-215° (from alcohol). Found: N 18.86; Cl 11.36%. Calculated for $C_{16}H_{16}N_4 \cdot HCl$: N 18.61; Cl 11.78%.

Acetaldehyde 1-methylbenzoimidazolyl-2-hydrazone was prepared similarly. Found: N 21.90; Cl 13.43%. Calculated for $C_{10}H_{12}N_4 \cdot HCl \cdot 2H_2O$: N 21.49; Cl 13.59%.

1-(1'-Benzylbenzoimidazolyl-2')-3-methyl-5-p-chlorophenylformazan (III). A solution of p-chlorophenyldiazonium chloride, prepared from 0.01 mole p-chloroaniline, 4 ml concentrated HCl, 20 ml water, and 0.01 mole sodium nitrite, was added to a cooled solution of 0.01 mole acetaldehyde 1-benzylbenzoimidazolyl-2-hydrazone in 40 ml alcohol. Then 2 N NaOH solution was added dropwise, and carefully, to bring the mixture to pH 5-6 (the cherry-red color characteristic of the Na salt of the formazan, must not appear), and the whole diluted with water until the formazan precipitated, kept for 2 hr at room temperature, and then the orange precipitate was filtered off and washed with water. The substance was soluble in alcohol, acetone, benzene, toluene, chloroform, dimethylformamide, solution shades varying from yellow to yellowish brown. It dissolved in alcoholic alkali to give a cherry-red coloration, reverting to yellow on acidification. If concentrated HCl was used for acidification, initially there was a brief deepening of the color, followed by decolorization. It crystallized well from alcohol.

The other formazans (I-XIV) were prepared similarly, using diazotization conditions known to be correct for each of the diazo-components employed.

The visible spectra of the compounds were measured with an SF-10 spectrophotometer, using a 10^{-4} M chloroform solution, layer thickness 3.05 mm (1.055 for compound XIV).

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Kirov Urals Polytechnic Institute, Sverdlovsk