SYNTHESIS OF 1,5-DIARYL-3-TETRAZOLYLFORMAZANS

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Several 1,5-diphenyl-3-tetrazolylformazans were synthesized by reaction of 1,5-diaryl-3-cyanoformazans with sodium azide.

1,5-Diarylformazans with electron-acceptor substituents in the 3 position form relatively stable complexes of the chelate type with a number of cations [1, 2], in connection with which they have found application as dyes and analytical reagents. Little study has been devoted to formazans with meso-heterocyclic substituents [3].

In the present research for the first time we have accomplished the synthesis of 1,5-diaryl-3-tetrazolyl formazans; we also studied some of their physicochemical characteristics.

The coupling of arenediazonium salts with the arylhydrazones of the corresponding heterocyclic aldehydes or compounds containing an active methylene group [3] is a method for the preparation of 1,5-diaryl-3-heterylformazans. However, the reaction of diazonium salts with tetrazolylacetic acid does not lead to the formation of 3-tetrazolylformazans. An attempt to obtain them through the arylhydrazones of tetrazolylacetic acid was also unsuccessful.

meso-Tetrazolylformazans (II, Table 1) were obtained by reaction of meso-cyanoformazans (I) with sodium azide in dimethylformamide (DMF) in the presence of ammonium chloride [4]. The reaction conditions depend on the structures of the starting meso-cyanoformazans: cyanoformazans with a sulfo group in the aromatic ring undergo cyclization to tetrazolylformazans under milder conditions (95°C) than formazans without these groups, for which the reaction temperature is 120°C.

On the basis of the IR spectroscopic data it may be concluded that neither the starting meso-cyanoformazans nor the tetrazolylformazans have chelate structures: the spectra of the compounds contain an absorption band of the stretching vibrations of the NH group of the tetraazo chain of a formazan at 3270-3450 cm^{-1}. Because of the formation of hydrogen bonds in formazans IIc-e, in which there are carboxyl and hydroxyl groups, this band is weakened considerably and is absent in the spectrum of formazan IIb. This is evidently why the band

TABLE 1. meso-Tetrazolylformazans

Compound	Appearance (crystallization solvent)	Found, %			Empirical formula	Calc., %			λ_{max}, nm (lg ε)	Yield, %
		C	H	N		C	H	N		
IIa	Orange prisms (ethanol)	57,5	4,0	37,8	$C_{14}H_{12}N_8$	57,5	4,1	38,3	252 (4,10); 296 (4,17); 439 (4,25)^a	60
IIb	Brown powder (DMF)	50,4	3,6	29,1	$C_{16}H_{12}N_8O_4$	50,5	3,2	29,5	212 (4,53); 297 (4,14); 434 (4,33)^b	50
IIc	Brown crystals (water)	31,9	2,8	21,4	$C_{14}H_{10}N_8Na_2O_8S_2$	31,8	1,9	21,2	270 (4,09); 294 (4,02); 489 (4,13)^c	70
IId	Red prisms (acetic acid)	28,0	1,8	18,8	$C_{14}H_8Cl_2N_8Na_2O_6S_2$	28,2	1,4	18,8	272 (4,09); 297 (4,03); 486 (4,19)^c	55
IIe	Red needles (methanol)	37,9	3,1	22,1	$C_{15}H_{11}N_8KO_6S \cdot CH_3OH$	38,2	3,0	22,3	270 (4,10); 296 (4,18); 476 (4,03)^c	30

a) In ethanol. b) In DMF. c) In water at pH 3.

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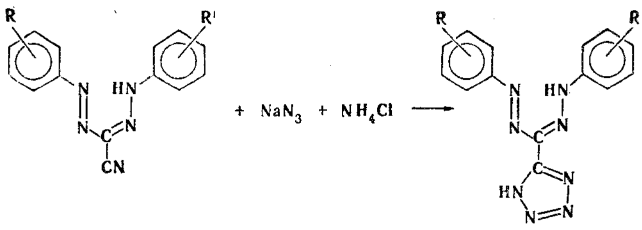
TABLE 2. Acid Dissociation Constants of Formazans I-II

Compound	pK_{a_1}(tetrazole NH)	pK_{a_2}(OH)	pK_{a_3}(OH)	pK_{a_4} (hydrazone NH)
IIc	4,98±0,05	7,74±0,06	9,24±0,04	11,26±0,08
Ic	—	6,65±0,03	8,28±0,04	11,80±0,08
IId	4,81±0,03	7,72±0,02	9,51±0,02	12,11±0,03
Id	—	5,98±0,05	8,74±0,04	11,13±0,08
IIe	4,83±0,08	5,18±0,08[a]	8,35±0,03	11,61±0,07
Ie	—	3,60±0,05[a]	7,40±0,05	11,11±0,05

a) This is the pK_a value of the COOH group.



Ia-e

IIa-e

I-II a $R = R' = H$; b $R = R' = 2\text{-}COOH$; c $R = R' = 2\text{-}OH\text{-}5\text{-}SO_3Na$;
d $R = R' = 2\text{-}OH\text{-}3\text{-}SO_3Na\text{-}5\text{-}Cl$; e $R = 2\text{-}OH\text{-}5\text{-}SO_3K$, $R' = 2\text{-}COOH$

of the NH stretching vibrations of the tetrazole appears in the spectra of phenyl-substituted formazans IIc-e in the form of weak absorption at 3075-3180 cm^{-1}. The conjugation of the two C=N groups shows up as intensification of the absorption bands at 1570-1595 cm^{-1} (tetrazole C=N) and the characteristic absorption of the tetrazole ring at 1040-1080 cm^{-1} [5]. Superimposition of the absorption bands is observed in the region of the stretching vibrations of azo groups at 1410-1440 cm^{-1} in the spectra of tetrazolylformazans II. The $C\equiv N$ absorption band at 2240-2250 cm^{-1} is absent in the spectra of cyclization products II.

The effect of the tetrazole ring on the pK_a values (Table 2) of the phenolic hydroxyl groups and carboxyl groups is manifested as a decrease in their acidities as compared with the starting 3-cyanoformazans (Ic-e) [6, 7]; this is probably due to the donor character of the tetrazole anion.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The electronic spectra were recorded with a Specord UV-vis spectrophotometer. Potentiometric titration was carried out with a TTT-2 titrator (Copenhagen) with CO_2-free 0.1 N KOH at an ionic strength ($NaNO_3$) of 0.1 at 20°C.

The starting formazans were obtained by the methods in [6-10].

meso-Tetrazolylformazans (II). A 0.01-mole sample of the corresponding meso-cyanoformazan I was dissolved in 30 ml of DMF, equimolar amounts of sodium azide and ammonium chloride were added, and the mixture was heated at 95°C for 16 h in the preparation of IIc-e and at 120°C in the preparation of IIa,b. The reaction mixture was then cooled and poured into 200 ml of water. The aqueous mixture was acidified to pH 2 with HCl, and the resulting precipitate was removed by filtration and crystallized from alcohol (IIa) or reprecipitated from DMF by the addition of water (IIb). In the case of IIc-e the reaction solution was filtered, and the solvent was removed from the filtrate by distillation at reduced pressure. The residue was dissolved in alcohol, and the solution was acidified with HCl. The mixture was vacuum evaporated, and the residue was crystallized from water (IIc), 50% acetic acid (IId), or alcohol (IIe).

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SYNTHESIS AND ABSORPTION SPECTRA OF 3,5-DIARYL-1,2,4-TRIAZOLES

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1,2,4-Triazoles with symmetrical tolyl substituents were obtained from the corresponding 1,3,4-oxadiazoles by reaction with formamide and subsequent hydrolysis of the resulting formyl derivatives; 1,2,4-triazoles with unsymmetrical substituents were obtained from iminoesters and hydrazides of acids. A set of bands of the triazole ring at 1470-1480, 1390, 1270-1290, 1140-1150, and 725-750 cm^{-1} and of NH vibrations at 2400-3200, 1580-1620, and 830-900 cm^{-1} are characteristic for the IR spectra of these triazoles. The UV spectra of the triazoles are characterized by phenyl ring absorption at about 200 nm and a band of electron transitions between the phenyl and triazole rings at 230-290 nm.

1,2,4-Triazole derivatives with various substituents (halo, nitro, amino, alkyl, and other groups) attached to the carbon atoms and one of the nitrogen atoms have been sufficiently adequately studied [1-4]. Not enough study has been devoted to triazoles with aromatic substituents attached to the heteroring carbon atoms.

We have synthesized a number of triazoles (Ia-p) with aromatic substituents in the 3 and 5 positions (Table 1). 3,5-Ditolyl-1,2,4-triazoles Ia,b were obtained by reaction of the easily accessible ditolyloxadiazoles [5, 6] with formamide and subsequent hydrolysis of the formyl derivatives [7]. We were unable to obtain 3,5-di(o-tolyl)-1,2,4-triazole by this method, possibly because of steric hindrance. Triazoles Ic-e were obtained by the method in [8]. Oxidation of the corresponding triazoles was used for the synthesis of 3,5-bis(carboxyphenyl)-1,2,4-triazoles If,g. Partial decomposition of the starting triazoles to give iso- or terephthalic acids occurs during the oxidation (they are the principal products in acidic media). Pure acids If,g were obtained by saponification of their esters (Ih-j). The dihydrazides (In,o) of the acids were also synthesized.

We investigated the IR and UV spectra of the synthesized compounds. The results of calculations of the vibrational spectra of triazole and its 3-chloro and bromo derivatives [4] and data from the spectroscopic studies of C-halogen-substituted triazoles and their potassium salts [9] were taken into account in the assignment of the frequencies in the IR spectra of the triazoles.

The bands of the NH stretching vibrations in the spectra of the investigated triazoles are found over a wide range of frequencies (2400-3200 cm^{-1}); this is due to the strong intermolecular association of these compounds. The bands at 1580-1620 and 830-900 cm^{-1} correspond to the NH deformation vibrations. A small long-wave shift of these bands is observed in the spectra of the N-deuterated products.

The heteroring vibrations are represented by an intense band at 1470-1480 cm^{-1}, absorption of medium intensity at 1390 cm^{-1}, and the most intense band at 1270-1290 cm^{-1}, which is

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