TETRAZOLE DERIVATIVES.

XI.* INVESTIGATION OF THE PROPERTIES AND TRANSFORMATIONS OF 1-(5-TETRAZOLYL)-3,5-DIPHENYLVERDAZYL

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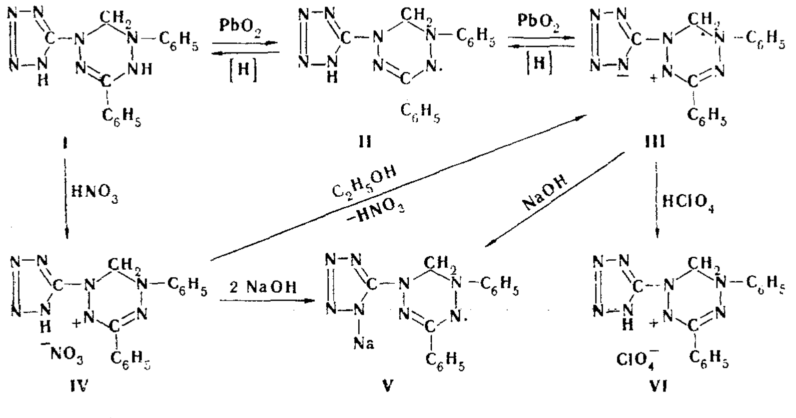
1-(5-Tetrazolyl)-3,5-diphenylverdazylium betaine was obtained by oxidation of the leuco base of 1-(5-tetrazolyl)-3,5-diphenylverdazyl under the influence of PbO_2 in acetone, whereas verdazylium nitrate, which is capable of undergoing conversion to the betaine, was obtained by oxidation with nitric acid. Both oxidation products in concentrated NaOH form the sodium salt of verdazyl, and the betaine adds perchloric acid to give verdazylium perchlorate.

Oxidation of the leuco base of 1-(5-tetrazolyl)-3,5-diphenylverdazyl (I) with lead dioxide in ether gives stable free radical II [1]. In other solvents – chloroform and acetone – the initially colorless solution of I takes on an intensely green color that gradually changes to violet. Moreover, the paramagnetic properties initially increase and then, as the color changes to violet, the ESR signal decreases until it disappears completely. The properties of the brown-violet products makes it possible to assign a 1-(5-tetrazolyl)-3,5-diphenylverdazylium betaine structure (III) to it. In fact, in contrast to II, the substance is insoluble in cold aqueous alkali, and the crystals and a solution of the crystals ($CHCl_3$) are diamagnetic. Betaine III is readily reduced in chloroform by hydroquinone and hydrogen over a Pd/$BaSO_4$ catalyst to give initially a blue-green paramagnetic solution of radical II, which is subsequently slowly decolorized, during which it loses its paramagnetism. Starting material I was obtained as a result of hydrogenation. It is interesting to note that in the absence of excess hydrogen, the catalyst used causes dehydrogenation of verdazyl I; after 3.5 min, an alcohol solution of it containing the catalyst takes on an intensely green color.

Diamagentic nitrate IV forms during oxidation of I with nitric acid in acetic acid.



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*See [1] for communication X.

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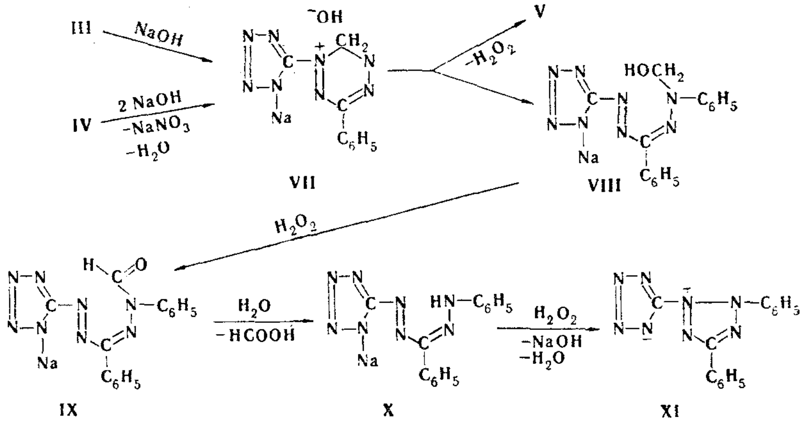
In contrast to the stable salts of triarylverdazyls [2], nitrate IV is capable of readily splitting out a molecule of nitric acid under the influence of nucleophilic agents (alcohol, water, and pyridine) to give betaine III. At the same time, betaine III in acetic acid is capable of adding perchloric acid to give the corresponding perchlorate (VI). Salts IV and VI readily dissolve in dilute aqueous alkali, from which verdazyl II (the purification of which, however, is difficult) is isolated by acidification with acetic acid. During the action of a 20% sodium hydroxide solution on salt IV, the latter is converted to the crystalline sodium salt (V) of verdazyl, which is intensely green. 1-(5-Tetrazolyl)-3,5-diphenylformazan X and 2-(5-tetrazolyl)-3,5-diphenyltetrazolium betaine XI are formed simultaneously in this reaction. Betaine III is capable of undergoing a similar reaction, but slight heating is required for this, otherwise the reaction proceeds slowly (8-10 h).



Intermediate VII, which is capable of undergoing conversion with the liberation of hydrogen peroxide to salt V and with ring opening to hydroxymethyl derivative VIII, is apparently formed in similar reactions. Formazan X, which is partially oxidized to tetrazolium salt XI, is formed by the oxidation of VIII to formyl derivative IX and subsequent hydrolysis of the latter.*

As compared with verdazyl II, one observes a greater contraction of the absorption line due to the stronger exchange interaction in crystals of salt V (singlet width 15.4 Oe for II and 11.1 Oe for V) in the ESR spectrum of sodium salt V (Fig. 1). A hyperfine structure (hfs) appears in the spectrum of a benzene solution of II.

The characteristic strong NH band of the verdazyl grouping at 3320 cm^{-1}, which vanishes on passing to radical II and betaine III, is present in the IR spectrum of I. The stretching vibrations of the NH group of the tetrazole ring, which usually cause a series of bands at 2500-2950 cm^{-1} [3], appear in the spectra of I, IV, and VI but are not observed in the case of II; this is apparently due to the formation of a strong intramolecular hydrogen bond between the tetrazole hydrogen and the N_2 atom of the tetrazine ring. The absorption at 3065-3069 cm^{-1} (I, II) and 3070-3110 cm^{-1} (III, IV) is associated with the stretching vibrations of aromatic C—H bonds, whereas the band at 2930-2960 cm^{-1} is associated with the CH_2 group of the verdazyl fragment [4].

The electronic spectra of radical II (Table 1) in various neutral solvents (benzene, dioxane, and acetone) remain almost unchanged with respect to the position of the absorption maxima, but a considerable decrease in the extinction of the long-wave absorption maximum is observed in the investigated series of solvents on passing from benzene to acetone. Ionization of the tetrazole ring in alkaline media causes a hypsochromic shift of the long-wave maximum ($\Delta\lambda_{max}$ 60 nm).

Betaine III is insoluble in benzene and dioxane; it dissolves in polar solvents to give violet solutions λ_{max} 562 nm in acetone and 550 nm in CH_3COOH). Salts IV and VI

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*The ability of 1-(5-tetrazolyl-3,5-diphenylformazan to undergo oxidation in alkaline media by hydrogen peroxide to tetrazolium salt XI is experimentally confirmed.

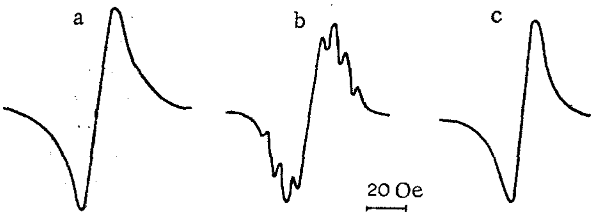

Fig. 1. ESR spectra: a) 1-(5-tetrazolyl)-3,5-diphenylverdazyl II in the crystalline state, $g_0 = 2.0027$; b) II in benzene solution (10^{-3} M), $g_0 = 2.0027$; c) sodium salt of 1-(5-tetrazolyl)-3,5-diphenylverdazyl V in the crystalline state, $g_0 = 2.0031$.

have similar coloration and spectra, and this constitutes evidence for the common character of the electronic structures of the tetrazine groupings in these three substances.*

EXPERIMENTAL†

The ESR spectra were obtained with an RÉ-1301 spectrometer. The IR spectra were recorded with a UR-20 spectrometer. The electronic spectra were recorded with SF-4A and SF-10 spectrophotometers.

1-(5-Tetrazolyl)-3,5-diphenylverdazylium Betaine (III). A) A solution of 1 g (3.3 mmole) of I in 60 ml of acetone was shaken for 15 min with 10 g of brown PbO_2, after which the mixture was filtered and concentrated in vacuo. The precipitated betaine (III) was removed by filtration to give 0.7 g (70%) of a product with mp 143° (dec.) as brown-violet threadlike crystals (from acetonitrile). The product was quite soluble in dimethylformamide (DMFA), only slightly soluble in alcohol, acetone, and chloroform, and insoluble in benzene and dioxane. Found: C 58.9; H 4.1; N 36.9%. $C_{15}H_{12}N_8$. Calculated: C 59.0; H 3.9; N 36.8%.

B) A 0.7-g (1.82 mmole) sample of IV was finely ground and placed in 50 ml of ethanol. The mixture was stirred at 20° for 1 h, after which it was filtered to give 0.55 g (100%) of long fibers (from ethanol) of III with mp 141.5° (dec.). No melting-point depression was observed for a mixture of this product with betaine III obtained in the preceding experiment. Found: N 36.9%. $C_{15}H_{12}N_8$. Calculated: N 36.8%.

1-(5-Tetrazolyl)-3,5-diphenylverdazylium Nitrate (IV). A 2.07-g (6.8 mmole) sample of I was dissolved at 40° in 20 ml of glacial acetic acid, after which the solution was cooled to 10°, and 12.4 ml of 26% HNO_3 was added. After 30 min, the resulting dark-violet precipitate was removed by filtration to give 1.82 g (70%) of a product with mp 120.5° (decomp.). Found: C 47.0; H 3.5; N 32.5%. $C_{15}H_{13}N_8 \times NO_3 \cdot H_2O$. Calculated: C 46.8; H 3.9; N 32.7%. Purification of the product by reprecipitation from acetic acid by the addition of carbon tetrachloride did not change the physical constants and composition of the product.

1-(5-Tetrazolyl)-3,5-diphenylverdazyl Sodium Salt (V). A) A 0.6-g (1.55 mmole) sample of nitrate IV was suspended in 20 ml of 20% NaOH, as a result of which the substance was converted to a shiny green product. The precipitate (A) was filtered, dried, washed with cold chloroform (three 20-ml portions), and dissolved by heating in 40 ml of $CHCl_3$ (B), after which the solution was filtered. The addition of 40 ml of

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*The assumption of splitting out of an acid molecule (HNO_3 or $HClO_4$) during the dissolving of IV and VI in CH_3COOH and the conversion to betaine III is not confirmed: the spectra of IV in CH_3COOH-concentrated HNO_3 (9:1) does not differ from the spectrum in CH_3COOH.

†With the participation of A. A. Skachilova and L. A. Zav'yalova.

TABLE 1. Electronic Spectra of I-VI

Compound	Solvent	λ_{max}, nm	log ε
I	Ethanol	230 305 — —	4,27 4,03 — —
II	Benzene	— 315* 380 690	— 4,11* 3,97 3,64
	Dioxane	260 315* 380 696	4,02 3,75* 3,48 3,11
		275 — — —	4,00 — — —
	Acetone	— — — 690	— — — 2,89
	0,1 *N* NaOH	265 315 370 630	3,90 3,51 3,34 3,23
	CH_3COOH	— 310 360 550	— 4,07 3,88 4,06
III	Acetone	— — — 562	— — — 4,00
	CH_3COOH	— 310 370* 540	— 4,00 3,50* 3,77
IV	CH_3COOH	— 305 360* 550	— 4,17 3,82* 4,00
V	Water	250 315* 376 650	4,18 3,64* 3,30 2,93
VI	CH_3COOH	— 310 360* 550	— 4,10 3,64* 3,84

*Inflection.

heptane precipitated product V from the solution. For purification, the substance was additionally reprecipitated from $CHCl_3$ by the addition of heptane to give 0.12 g (23%) of V with mp 163° (decomp.) as fine green prisms. Found: C 52.0; H 4.3; N 32.5%. $C_{15}H_{12}N_8Na \cdot H_2O$. Calculated: C 52.2; H 4.1; N 32.4%. The product was readily soluble in water, acetone, and alcohol but insoluble in benzene.

Acidification of the filtrate after precipitation (A) gave 0.05 g of 1-(5-tetrazolyl)-3,5-diphenylformazan X with mp 147° (dec.) as dark-red prisms from ethanol. No melting-point depression was observed for a mixture of this product with an authentic sample [5]. The chloroform solution (B) obtained by cold washing of salt V was concentrated, and a precipitate was formed from it by the addition of heptane. The precipitate was washed with water to give 0.1 g of 2-(5-tetrazolyl)-3,5-diphenyltetrazolium betaine XI with mp 207° (dec.) as colorless needles from ethanol. No melting-point depression was observed for a mixture of this product with an authentic sample [5].

B) A 1-g (3.3 mmole) sample of betaine III was treated with 30 ml of 20% NaOH at 35-40°. The reaction products were isolated as in the manner described above. The yield of salt V with mp 163° (decomp.) was 0.15 g (13%). No melting-point depression was observed for a mixture of this product with the salt obtained from experiment A. Found: N 32.4%. $C_{15}H_{12}N_8Na \cdot H_2O$. Calculated: N 32.4%. Workup also yielded 0.1 g of X and 0.15 g of XI.

1-(5-Tetrazolyl)-3,5-diphenylverdazylium Perchlorate (VI). A 0.1-g (0.33 mmole) sample of betaine III was dissolved by heating in 3.5 ml of acetic acid, after which the solution was cooled and treated with 0.12 ml of 30% $HClO_4$. The mixture was cooled for 1 h, after which it was filtered to give 0.07 g (50%) of a product with mp 144° (decomp.) as dark-violet prisms. Found: C 43.0; H 3.4; N 26.6%. $C_{15}H_{13}N_8 \cdot ClO_4 \cdot H_2O$. Calculated: C 42.6; H 3.6; N 26.5%. IR spectrum: 1591, 1540 cm^{-1} (C=C, C=N).

Reduction of Betaine III. Hydrogen was bubbled into a suspension of 1 g of betaine III and 0.3 g of a $Pd/BaSO_4$ catalyst in 90 ml of ethanol. After 5 min, the violet solution changed to a green solution, which was decolorized as hydrogen was bubbled through it for 2 h. The mixture was filtered, and the solution was concentrated in vacuo to give 0.8 g (80%) of leuco base I with mp 176.5° (decomp.) as colorless needles from chloroform. No melting-point depression was observed for a mixture of this product with a genuine sample. Found: N 36.8%. $C_{15}H_{14}N_8$. Calculated: N 36.6%. IR spectrum: 3319 cm^{-1}(NH).

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