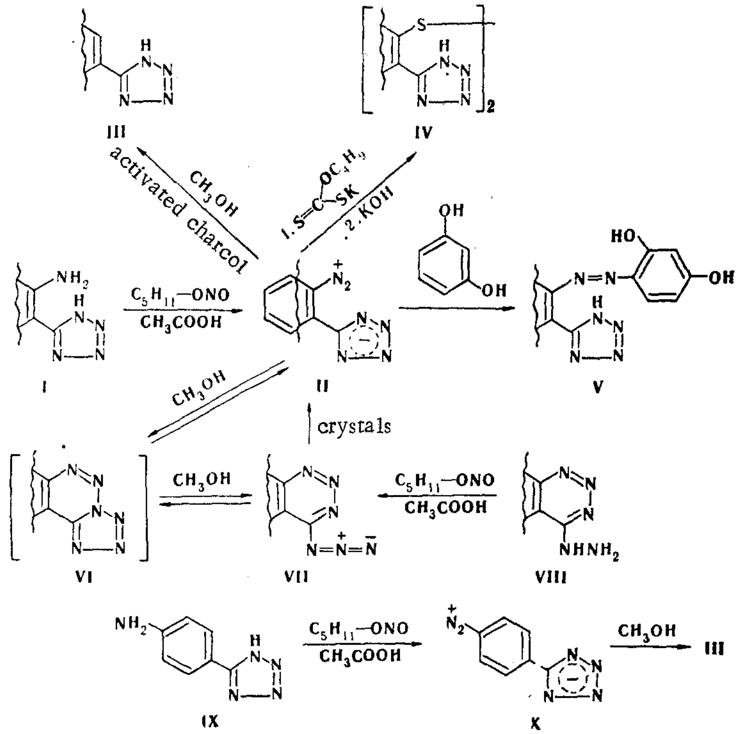
RING-CHAIN TAUTOMERIC TRANSFORMATIONS OF THE PRODUCT OF DIAZOTIZATION OF 5-(2'-AMINOPHENYL)TETRAZOLE

B. V. Golomolzin, I. Ya. Postovskii,*
L. G. Egorova, and N. M. Perova

UDC 547.796.1'872:541.623:542.958.3

It was established on the basis of IR spectral data that the products of the reaction of 5-(2'-aminophenyl)tetrazole and 4-hydrazinobenzo-1,2,3-triazine with amyl nitrite have the 5-(2'-diazoniaphenyl)tetrazolestructure in the crystalline state. A study of the UV spectra of the latter showed that in methanol solution it exists in equilibrium with the isomeric 4-azidobenzo-1,2,3-triazine.

Ring-chain tautomerism with reversible cleavage of the N-N bond is constantly attracting the attention of researchers engaged in the study of heterocycles that contain many nitrogen atoms. Double tautomerism of the imidazo[4,5-e]tetrazolo[1,5-c]-1,2,3-triazine system has been described [1]. One's attention is drawn to the possibility of the formation of the labile benzo[e]tetrazolo[1,5-c]-1,2,3-triazine system by diazotization of 5-(2'-aminophenyl)tetrazole.



A product that has the 5-(2'-diazoniaphenyl)tetrazole (II) structure in the crystalline state was isolated by the action of amyl nitrite in acetic acid on 5-(2'-aminophenyl)tetrazole (I). The IR spectrum of II contains an absorption band of a diazo group at 2283 cm^{-1}, and only signals of aromatic protons are observed in its PMR spectrum; this constitutes evidence for the absence of an external acetate anion. Reactions that are typical for diazo compounds are characteristic for II: elimination of the diazo group in methanol in the presence of activated charcoal gives 5-phenyltetrazole (III), the reaction with potassium butyl-

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*Deceased.

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk 62002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1557-1559, November, 1981. Original article submitted February 18, 1981.

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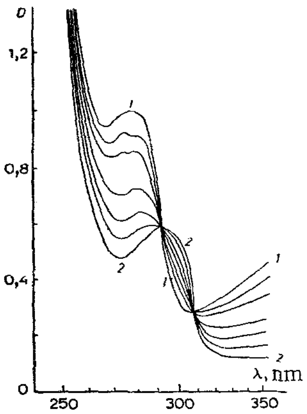

Fig. 1. UV spectra of II in methanol (initial concentration $1.86 \cdot 10^{-4}$ mole/liter): 1) spectrum immediately after dissolving; 2) final spectrum (the intermediate spectra were recorded at 1 h intervals).

xanthate and subsequent alkaline hydrolysis lead to bis[(2'tetrazol-5-yl)phenyl] disulfide (IV), and diazo coupling product V is formed with resorcinol.

When II is allowed to stand in methanol solution, its UV spectrum gradually changes: Isobestic points are observed (Fig. 1), and the intensities of the maxima at 238 and 368 nm decrease. After 6 h, the spectrum undergoes no further changes. Compound II can be isolated unchanged from this solution after evaporation of the solvent, and this refutes the assumption that II undergoes deazotization to give 5-phenyltetrazole (III); in addition, absorption above 270 nm is absent in the spectrum of III. The most probable explanation for the observed transformation is two-step conversion of II through the unstable benzo[e]tetrazolo[1,5-c]-1,2,3-triazine (VI) to 4-azidobenzo-1,2,3-triazine (VII). An isomer of II, viz., 5-(4'-diazoniaphenyl)tetrazole (X), which was synthesized from 5-(4'-aminophenyl)tetrazole (IX), contains the same (as in the case of II) absorption band of a diazo group (2272 cm^{-1}, in the crystalline state) in its IR spectrum, and the absence of absorption of an ionized carboxy group at 1650-1700 cm^{-1} indicates the absence of an external acetate anion. In methanol solution X is gradually converted to III: The UV spectrum of X after dissolving in methanol gradually changes and becomes identical to the spectrum of III after 24 h.

The reaction of 4-hydrazinobenzo-1,2,3-triazine (VIII) with amyl nitrite in acetic acid has been described [2], and structure VII was assigned to the product in the crystalline state. In a repetition of this synthesis we isolated a product with the same spectral characteristics as the compound obtained in [2]. This product was identical to the product of diazotization of 5-(2'aminophenyl)tetrazole, and the UV spectrum of a solution of it in methanol underwent the same changes. These results make it possible to conclude that both I and VII form the same compound upon reaction withamyl nitrite; the product has structure II in the crystalline state, and the $II \rightleftarrows VI \rightleftarrows VII$ equilibria are established when it is dissolved in methanol.

EXPERIMENTAL

The IR spectra of mineral oil pastes of II and X were recorded with a UR-20 spectrometer with LiF and NaCl prisms. The UV spectra of II, III, and X were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of II and V in DMSO were recorded with a Perkin-Elmer R12-B spectrometer (60 MHz) with tetramethylsilane as the internal standard.

5-(4'-Aminophenyl)tetrazole (IX). A mixture of 6 g (31 mmole) of 5-(4'nitrophenyl)-tetrazole [3], 10 g (170 mmole) of hydrazine hydrate, 5 g of SKT activated charcoal, and 90 ml of ethanol was refluxed for 12 h, after which the hot reaction mixture was filtered to remove the charcoal, and the solvent was removed from the filtrate by distillation to dryness. The residue was dissolved in hot water, the solution was neutralized to pH 6 with HCl and cooled, and the resulting precipitate of IX was removed by filtration and crystallized from water to give 2.6 g (52%) of colorless needles with mp 266-267°C (mp 268-270°C [4]).

5-[2'-(4')-Diazoniaphenyl]tetrazoles (II, X). A 1-g (6 mmole) sample of I [5] or IX was mixed with 10 ml of glacial acetic acid, the mixture was cooled to 5°C, and 1.2 g (10 mmole) of freshly distilled amyl nitrite was added. The reaction mixture was maintained at 5°C overnight, and the precipitated II or X was removed by filtration, washed with a small amount of cold methanol, and dried *in vacuo* without heating. The yield of II and X was 0.6

g (58%). The product was crystallized from methanol without the addition of charcoal. Compounds II and X exploded when they were heated, and this made it impossible to subject them to elementary analysis.

5-(2'-Diazoniaphenyl)tetrazole (II) was obtained as yellow crystals that decomposed explosively at 120°C. IR spectrum: 2283 cm^{-1} (diazo group). PMR spectrum: 8.30 and 8.70 ppm (m, benzene ring protons). UV spectrum recorded immediately after dissolving in methanol, λ_{max} ($\varepsilon \cdot 10^{-3}$): 238 (20.96), 282 (5.32), and 368 nm (2.28). An identical product with the same spectral characteristics was obtained by the reaction of VIII with amyl nitrate in acetic acid by the method in [2].

5-(4'-Diazoniaphenyl)tetrazole (X) was obtained as yellow crystals that decomposed explosively at 115°C. IR spectrum: 2272 cm^{-1} (diazo group). UV spectrum recorded immediately after dissolving in methanol, λ_{max} ($\varepsilon \cdot 10^{-3}$): 240 (20.38) and 333 nm (9.95). After 24 h, the UV spectrum of a solution of the product was identical to the spectrum of 5-phenyltetrazole (III).

Deazotization of II. A 0.3-g (2 mmole) sample of II was dissolved in 10 ml of refluxing methanol, 0.1 g of activated charcoal was added, and the mixture was refluxed for 5 min. The charcoal was removed by filtration, the filtrate was evaporated to dryness, and the residual III was crystallized from water to give 0.15 g (48%) of a substance that did not depress the melting point of 5-phenyltetrazole obtained from benzonitrile by the method in [3]. UV spectrum (in methanol, λ_{max} ($\varepsilon \cdot 10^{-3}$): 205 (16.26) and 240 nm (14.33).

Bis[(2'-tetrazol-5-yl)phenyl] Disulfide (IV). A 1.5-g (9 mmole) sample of II was added in portions with stirring at 20°C to a solution of 1.7 g (11 mmole) of potassium butylxanthate in 30 ml of methanol, and the mixture was stirred at 20°C for 1 h. The small amount of undissolved impurities was removed by filtration, the methanol was removed by distillation, and the oily residue was refluxed in 20 ml of 10% KOH solution for 1 h. The resulting solution was acidified to pH 1 with concentrated HCl, and the oily precipitate, which solidified on standing, was crystallized from aqueous ethanol (1:1) containing charcoal to give 0.8 g (50%) of colorelss crystals of IV with mp >250°C. The IR spectrum of the product did not contain an absorption band of an SH group at 2550-2600 cm^{-1}. Found: C 48.0; H 3.1; N 32.1; S 18.1%. $C_{14}N_{10}N_8S_2$. Calculated: C 47.5; H 2.8; N 31.7; S 18.1%.

1-(5-Tetrazolyl)-2',4'-dihydroxyazobenzene (V). A solution of 3.4 g (20 mmole) of II in 50 ml of methanol was added in portions to a solution of 3.3 g (30 mmole) of resorcinol in 50 ml of methanol, and the reaction mixture was refluxed for 30 min. It was then cooled, and the precipitated V was removed by filtration. Dilution of the filtrate with a twofold amount of water gave an additional amount of V for an overall yield of 3.4 g (54%). The product was purified by reprecipitation from alcohol solution by the addition of water. The dark-red precipitate had mp 250°C. PMR spectrum: 6.40 and 6.61 (m, 3-H', 5-H', 6-H'); 7.70 and 8.05 ppm (m, 3-H, 4-H, 5-H, 6-H). Found: N 26.4%. $C_{13}H_{10}N_6O_2 \cdot CH_3OH$. Calculated: N 26.7%. A solution of V was decolorized by the action of sodium hydrosulfite, and this confirmed the presence of an azo grouping.

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