and the mixture heated at 100°–120° C for about an hour, after which the reaction products were cooled and extracted with ether. The ether extract gave 20 g (64%) IV. Found: C 53.39, 53.56; H 8.95, 8.96; Si 17.30, 17.52%. Calculated for $C_7H_{14}SiO_2$: C 53.13; H 8.92; Si 17.70%. Silalactone XIV was prepared similarly.

Si-Dimethyl-1-methyl-3-silavalerolactam (VII). 8.2 g NaOMe in 50 ml dry MeOH was added to 10 g VI, and the mixture refluxed for 1 hr. The precipitate of NaCl was filtered off, and the MeOH distilled off from the filtrate, to give, on vacuum-distilling the residue, 6.6 g (81.5%) VII. Found: C 53.20, 53.42; H 9.57, 9.74; Si 17.22, 17.41; N 9.3, 9.1%. Calculated for $C_7H_{15}SiNO$: C 53.45; H 9.61; Si 17.85; N 8.9%.

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RESEARCHES ON TETRAZOLE AND s-TRIAZOLE FORMAZANS

II. Synthesis and Colors of 1-(1'-Phenyltetrazolyl)-5-arylformazans Containing Nitro and Dimethylamino Groups*

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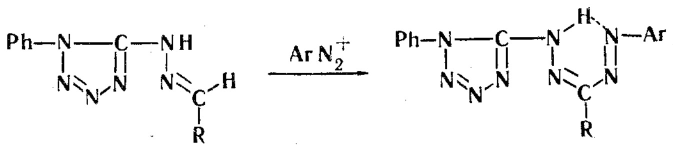
New 1-(1'-phenyltetrazolyl)-5-arylformazans are synthesized, and their IR and visible region spectra are investigated. The effects of electron-donating and -accepting groups on the colors of the formazans and on the stability of intramolecular hydrogen bonding of the formazyl ring are elucidated.

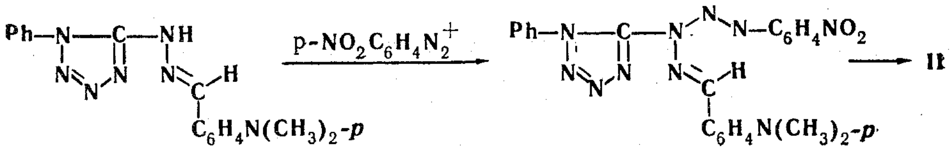
In further investigating the relationship between structure and color of formazans having a heteroaromatic group at N_1, it was of interest to study the effects of para electron-donating and -accepting groups in aryl groups at C_3 and N_5. In this connection, 1-(1'-phenyltetrazolyl)-5-arylformazans (II) with R and Ar containing p-nitro and p-dimethylamino groups have now been synthesized.

The formazans were prepared by coupling arylidiazonium salts with 1-phenyltetrazolyl-5-hydrazones (I, with R = Me, Ph, $PhNO_2$, $PhNMe_2$) in ethanolic alkali, pyridine, or mixed pyridine-ethanol in the presence of alkali:



I II

The low yield of formazan XI (table) is striking. Apparently, this is due to the electron-donor group Me_2N, present in the phenyl group of the hydrazone Ia, giving rise to a high electron density at the imino nitrogen, thus facilitating electrophilic substitution with formation of an intermediate product, the tetrazene III, but simultaneously the aldehyde hydrogen acquires low mobility, and rearrangement of the tetrazene to formazan is hindered (cf. [2]).



Ia III

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* For Part I see [1].

The IR spectra of the formazans prepared were measured using crystals suspended in vaseline, and it was found that in the compounds with a methyl group at C_3, the formazyl group is not locked to the ring (and we previously demonstrated that this was also true of other C-methylphenyltetrazolylformazans [1]). This was deduced from the fact that these formazans exhibit a well-defined absorption band in the 3200–3300 cm^{-1} region, which must be ascribed to valence vibrations of the N–H group. With the exception of compound VII, formazans with an aryl group at C_3 do not give the NH band, and in all probability have a closed quasi-heteroatomic formazyl ring due to stable intramolecular bonding. Formazan VII, with phenyl at C_3 and p-nitrophenyl at N_5, has an open formazyl group, since the IR spectra have an NH band at 3200 cm^{-1}. Apparently, a NO_2 group in this compound attracts the lone electron pair at the N_5 nitrogen atom, thus reducing the possibility of formation of a stable chelate quasi-heteroatomic ring. The red color of this formazan also indicates its open structure; other formazans with aryl at C_3, are much more deeply colored (see table).

To determine the effects of nitro and dimethylamino groups on the colors of the formazans prepared, their visible spectra were also investigated. The results given in the table show that replacement of methyl at position 3 by phenyl shifts λ_{max} bathochromically. Introduction of nitro or dimethylamino at position 3 or 5 in the phenyl group gives rise to a considerable bathochromic shift. The maximum effect is shown by a nitro group, particularly if it is present in phenyl at N_5. When the dimethylamino group is introduced into the phenyl group with the latter at position 5 (compounds III, VI, X), the intensity of absorption increases; but if this group is at position 3 in the phenyl group, the intensity of absorption considerably decreases (compounds VIII, XI). These results reflect the role of conjugation between groups at N_1 and N_5 via the formazyl system of bonds, and at the same time they indicate the reciprocal effects of the groups at positions C_3 and N_5. It is to be mentioned that the formazans prepared exhibit positive solvatochromism, and form complexes with copper and nickel; this will be the subject of a separate communication.

Experimental

1-(1'-Phenyltetrazolyl)-5-p-nitrophenyl-3-phenylformazan (VII). A solution of 0.5 g NaOH in 10 ml water was added to 1 g (0.005 mole) benzaldehyde-1-phenyltetrazolyl-5-hydrazone (mp 210° C [3]) suspended in 40 ml EtOH. The resultant solution was cooled to 0°–2° C, a solution of p-nitrophenylenediazonium salt (prepared from 0.69 g p-nitroaniline, 3 ml conc. HCl, 0.38 g $NaNO_2$, and 10 ml H_2O) added, and the reaction mixture left overnight, then the formazan filtered off, carefully washed first with water, then with a small amount of EtOH. The other results are given in the table. Formazans IV, V, VI were prepared similarly.

1-(1'-Phenyltetrazolyl)-5-phenyl-3-p-nitrophenylformazan (IX). 0.5 g (0.0016 mole) p-nitrobenzaldehyde phenyltetrazolylhydrazone was dissolved in 20 ml pyridine and 20 ml EtOH, the solution cooled to 0°–4° C, and the phenyldiazonium solution prepared from 0.2 g aniline, 0.6 ml conc. HCl, 2 ml water, and 0.17 g $NaNO_2$, added. Formazan X was prepared similarly.

1-(1'-Phenyltetrazolyl)-5-phenyl-3-p-dimethylaminophenylformazan (VIII). 0.6 g (0.002 mole) p-dimethylaminobenzaldehyde phenyltetrazolylhydrazone was dissolved in 20 ml EtOH plus 10 ml pyridine, and a solution of 0.25 g NaOH in 5 ml water added. The resultant hydrazone solution was coupled with diazotized aniline.

The formazan XI was prepared similarly.

It should be mentioned that all the formazans were difficult to burn when carrying out the elementary analyses, and apparently this is connected with the large number of nitrogen atoms in the ring.

The IR spectra were observed with an IKS-14 instrument, LiF prism, using a paste with vaseline. Visible region spectra were measured with a SF-10 spectrophotometer, in $CHCl_3$ solution, concentration 10^{-4} M.

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