REACTION OF HETEROCYCLIC DIAZONIUM SALTS WITH HYDRAZONES

L. M. Shegal and I. L. Shegal

UDC 547.789.6'79:542.958.3

Depending on the nature of the heteroring and the hydrazone, a formazan or a heterylazophenylhydrazone are formed in the reaction of an aryl hydrazone with the diazonium salt obtained from a heterocyclic amine. Disproportionation to form a triphenylformazan is also possible.

One of the methods for obtaining unsymmetrical formazans that contain heterocyclic residues is coupling of a heterocyclic diazonium salt with an aryl hydrazone. This method was used to obtain formazans containing thiazolyl [1] and benzothiazolyl [2] residues, and, in the latter case, benzaldehyde benzothiazolylazophenylhydrazone was isolated along with the formazan on coupling with benzaldehyde phenylhydrazone.

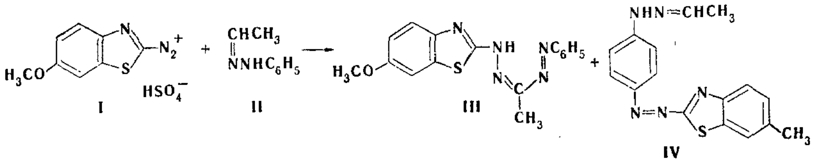
Since a considerable number of heterocyclic amines are capable of forming diazonium salts, it seemed of interest to study the possibility of obtaining unsymmetrical formazans of the heterocyclic series from the corresponding heterocyclic amines. Continuing our investigations in this area, we established that, as in the case of benzaldehyde phenylhydrazone, a mixture of substances, from which acetaldehyde 4-(6-methoxy-2-benzothiazolylazo)phenylhydrazone (IV) was isolated along with N-(6-methoxy-2-benzothiazolyl)-3-methyl-N'''-phenylformazan (III), is formed in the reaction of 6-methoxy-2-benzothiazolediazonium sulfate (I) with acetaldehyde phenylhydrazone (II). Compound IV, which is obtained owing to the increased electrophilicity of the diazonium salt (I), differs from III in that it is incapable of forming complexes with metal salts and gives the characteristic blue color associated with salt formation and transition to the quinoid form in acid media.

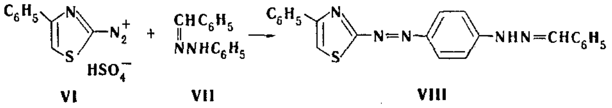
An attempt to obtain N-(4-phenyl-2-thiazolyl)-3,N'''-diphenylformazan (V) by coupling 4-phenyl-2-thiazolediazonium sulfate (VI) with benzaldehyde phenylhydrazone (VII) resulted in the formation of a mixture, from which only benzaldehyde 4-(4-phenyl-2-thiazolylazo)phenylhydrazone (VIII) could be isolated. This conclusion is corroborated by the ability of VIII to give a blue color in both acid and alkaline media, together with the fact that it remains unchanged on mixing with metal salts. In our opinion, the deepening of the color in acidic and alkaline media is associated with the formation of ions of the quinoid type that are similar in structure. Authentic V, obtained by the action of a benzenediazonium salt on benzaldehyde 4-phenyl-2-thiazolylhydrazone (IX), is more deeply colored than the isomeric VIII and readily forms complexes with metal salts in the cold.

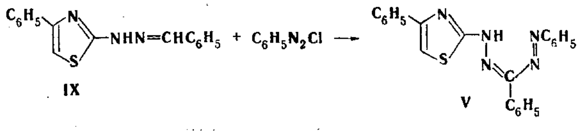
We also isolated 1,3,5-triphenylformazan (XII) in addition to N-(1,2,4-triazolyl-3-)-3,N'''-diphenylformazan (XI) in the reaction with VII of diazonium salt X, obtained from 3-amino-1,2,4-triazole. The reaction of VII with tetrazolediazonium salt (XIII) proceeds exclusively to favor formation of XII. The mechanism of this unusual transformation apparently consists in the initial formation of an azolyldiphenylformazan, which is unstable in acid media and is cleaved to form a benzenediazonium salt, which also attacks the unchanged starting hydrazone (VII).

It is interesting to note that both diazonium salts (X and XIII) form N-(1,2,4-triazolyl-3-)- (XIV) and N-(tetrazolyl-5)-3-methyl-N'''-phenylformazans (XV), respectively, on reaction with II. Both formazans (XIV and XV) are light-yellow compounds that give characteristic deepening of the coloration in alkaline media and form complexes with Cu^{2+}, Ni^{2+}, and Co^{2+} in alcohol solution.

N. P. Ogarev Mordovskii State University, Saransk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1062-1064, August, 1972. Original article submitted July 12, 1971.







EXPERIMENTAL

N-(6-Methoxy-2-benzothiazolyl)-3-methyl-N‴-phenylformazan (III) and Acetaldehyde 4-(6-Methoxy-2-benzothiazolylazo)phenylhydrazone (IV). A solution of a diazonium salt obtained from 0.72 g (4 mmole) of 6-methoxy-2-aminobenzothiazole, 15 ml of 60% H_2SO_4, and 0.28 g (4 mmole) of $NaNO_2$ in 10 ml of water was added at 0° to a solution of 0.54 g (4 mmole) of II in 40 ml of ethanol, and the mixture was stirred for 15 min. The pH was brought up to 6-7 by the addition of 2 N NaOH, and the mixture was allowed to stand at 0° for 24 h. The precipitate was removed by filtration, washed with water, and chromatographed with a column packed with aluminum oxide to give 0.33 g (25%) of III with mp 87-88°. Found: C 58.7; H 5.0; N 21.0%. $C_{16}H_{15}N_5OS$. Calculated: C 59.1; H 4.7; N 21.5%. λ_{max}, nm: in alcohol 438, in alcoholic alkali 526; complexes (in alcohol) with Zn^{2+} 520, Cu^{2+} 660, and Co^{2+} 538. Subsequent elution yielded 0.26 g (20%) of IV with mp 69-70° (red plates). Found: C 59.4; H 4.9; N 21.8%. $C_{16}H_{15}N_5OS$. Calculated: C 59.1; H 4.7; N 21.5%.

Benzaldehyde 4-(4-Phenyl-2-thiazolylazo)phenylhydrazone (VIII). A solution of a diazonium salt obtained from 1.76 g (0.01 mole) of 4-phenyl-2-aminothiazole, 0.69 g (0.01 mole) of $NaNO_2$, and 10 ml of 60% H_2SO_4 was added at 0° to a solution of 1.96 g (0.01 mole) of benzaldehyde phenylhydrazone (VII) in 20 ml of dimethylformamide and 10 ml of pyridine, and the mixture was allowed to stir for 15 min. The pH was brought up to 3.5 by the addition of 2 N NaOH, and the mixture was allowed to stand at 0° for 24 h. The mixture was then diluted with water, and the resulting precipitate was removed by filtration, chromatographed with a column filled with aluminum oxide, and crystallized from chloroform to give 0.4 g (10%) of VIII with mp 229-230° (green plates). λ_{max}, nm: in alcohol 516, in alcoholic alkali 640, in hydrochloric acid 650. Found: C 69.3; H 4.8; N 17.9%. $C_{22}H_{17}N_5S$. Calculated: C 68.9; H 4.5; N 18.3%.

N-(4-Phenyl-2-thiazolyl)-3,N‴-diphenylformazan (V). A diazonium salt solution obtained from 0.93 ml (0.01 mole) of aniline and 0.69 g (0.01 mole) of $NaNO_2$ in 10 ml of 10% HCl was added at 0° to 2.8 g (0.01 mole) of IX in 50 ml of dimethylformamide and 15 ml of pyridine. The pH was brought up to 6 by the addition of sodium acetate, and the mixture allowed to stand at 0° for 24 h. The mixture was diluted with water, and the precipitated V was removed by filtration to give 0.54 g (14%) of a compound with mp 166-168° (needles from aqueous ethanol). λ_{max}, nm: in alcohol 578, complex (in alcohol) with Cu^{2+} 660, Ni^{2+} 610. Found: C 68.6; H 4.5; N 17.8%. $C_{22}H_{17}N_5S$. Calculated: C 68.9; H 4.5; N 18.3%.

N-(1,2,4-Triazol-3-yl)-3,N‴-diphenylformazan (XI) and 1,3,5-Triphenylformazan (XII). A solution of X obtained from 0.84 g (0.01 mole) of 3-amino-1,2,4-triazole and 0.69 g (0.01 mole) of $NaNO_2$ in 10 ml of 60% H_2SO_4 was added at 0° to 1.96 g (0.01 mole) of VII in 75 ml of ethanol and 25 ml of pyridine. The pH was brought up to 5 by the addition of sodium acetate, and the mixture was allowed to stand at 0° for 24 h. The red reaction mass was diluted with 200 ml of water, and the mixture was filtered. Chromatography with a column packed with aluminum oxide with elution by chloroform gave 0.6 g (21%) of XII with mp 173° [3]. The second fraction yielded 0.58 g (20%) of XI with mp 118-121°. λ_{max}, nm: in alcohol 466, in alcoholic alkali 496, complex (in alcohol) with Cu^{2+} 590, Ni^{2+} 600, Co^{2+} 640. Found: C 62.1; H 4.6; N 33.2%. $C_{15}H_{13}N_7$. Calculated: C 61.8; H 4.5; N 33.7%.

Reaction of Tetrazolediazonium Salt (XIII) with VII. A solution of XIII obtained from 0.425 g (5 mmole) of aminotetrazole, 12.5 ml of 30% H_2SO_4, and 3.5 ml (5 mmole) of 10% $NaNO_2$ solution was added at 0° to 0.98 g (5 mmole) of VII in 40 ml of ethanol and 10 ml of pyridine. Sodium acetate (8 g) was added to bring the pH up to 3.5, and the mixture was allowed to stand at 0° for 24 h. Dilution with water yielded 0.25 g (17%) of XII with mp 172-173°.

N-(1,2,4-Triazolyl-3)-3-methyl-N'''-phenylformazan (XIV). A solution of X obtained from 0.84 g (0.01 mole) of aminotriazole in 15 ml of glacial acetic acid, 0.69 g (0.01 mole) of $NaNO_2$, and 10 ml of 60% H_2SO_4 was added at 0° to 1.34 g (0.01 mole) of II in 70 ml of ethanol and 15 ml of pyridine. The pH was brought up to 5 by the addition of sodium acetate, and the mixture was diluted with water after 24 h to give 1.14 g (40%) of light-yellow XIV with mp 215-218° (prisms from aqueous ethanol). λ_{max}, nm: in alcoholic alkali 530, complex (in alcohol) with Cu^{2+} 570, Ni^{2+} 410, 578, and Co^{2+} 420, 630. Found: C 45.2; H 5.3; N 36.6%. $C_{10}H_{11}N_7 \cdot 2H_2O$. Calculated: C 45.3; H 5.7; N 37.0%.

N-(5-Tetrazolyl)-3-methyl-N'''-phenylformazan (XV). The reaction of XIII with II was carried out the same way as with VII, and the yield of XV with mp 158-160° (prisms from alcohol) was 46%. λ_{max}, nm: in alcohol 428, in alcoholic alkali 510, complex (in alcohol) with Cu^{2+} 544, Ni^{2+} 412, 570, and Co^{2+} 420, 640. Found: C 46.7; H 4.3; N 48.8%. $C_9H_{10}N_8$. Calculated: C 47.0; H 4.4; N 48.7%.

LITERATURE CITED

1. W. Ried, H.Gick, and G.W.Oertel, Ann.,581, 36 (1953).
2. L. M. Shegal, I. L. Shegal, and N. P. Bednyagina, Khim. Geterotsikl. Soedin., 35 (1972).
3. H. V. Pechmann, Ber., 27, 1690 (1894).