DMF. Yield 0.18 g (15%), mp 250-251°C (dec.). Found: C 65.1; H 6.2; N 16.4%. $C_{14}H_{13}N_3O_2$. Calculated: C. 65.4; H 5.9; N 16.3%. The compound was identical to that described in [5].

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REACTION OF N-AMINOBENZIMIDAZOLIUM CATIONS WITH AROMATIC ALDEHYDES. SYNTHESIS OF 2,4-DIARYL-as-TRIAZINO[1,6-a] BENZIMIDAZOLES

V. V. Kuz'menko, T. A. Kuz'menko, and A. M. Simonov

UDC 547.785.5'873'571:542.953.4:543.422

On heating with aromatic or heteroaromatic aldehydes in polar aprotic solvents, 1-amino-3-alkylbenzimidazolium salts form 2,4-diaryl derivatives of a new heterocyclic system of as-triazino[1,6-a]benzimidazole.

The reaction of 1-amino-3-alkylbenzimidazolium salts (I) with aromatic aldehydes in an alcoholic medium leads to the usual Schiff base analogs II in high yields [1]. We found that in boiling DMFA, DMSO, or HMPTA, at 150°C, this process is more complex in character and is accompanied by the formation of 2,4-diaryl derivatives of a new heterocyclic system — as-triazino[1,6-a]benzimidazole (III). With ketones and 2-methyl derivatives of salts I, the reaction does not proceed. According to our data, examples of this type of transformations are not known for N-amino derivatives of heterocycles. The present work was undertaken to establish the structure of compounds III and the factors influencing their formation (the structural features of cations II, temperature conditions, basicity of medium).

Examination of the PMR spectra of the non-salt-like bright-yellow compounds, which we isolated, showed clearly that at one of the reaction stages, salts I undergo dealkylation (absence of signals in the absorption region of the aliphatic protons in the spectrum of IIIa). Moreover, the more simple in character spectra of the model compounds IIIb,c, obtained from salts Ia,c with anisaldehyde, unequivocally indicated that compounds III include two aldehydic residues in their composition. This was confirmed by the data of the elemental analysis and mass spectrometric determination of the molecular weight. In the PMR spectrum of compound IIIb two singlets of the methyl group are observed in the region of 3.70 and 3.75 ppm, four doublets of the aromatic protons at 6.82, 6.90, 8.23, and 9.0 ppm, with SSCC (spin–spin coupling constant) of 9.0 Hz, which are assigned to ortho- and meta-protons of two benzene rings, and also two multiplets of the benzimidazole ring protons in the region of 7.35 and 7.90 ppm

Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344006.

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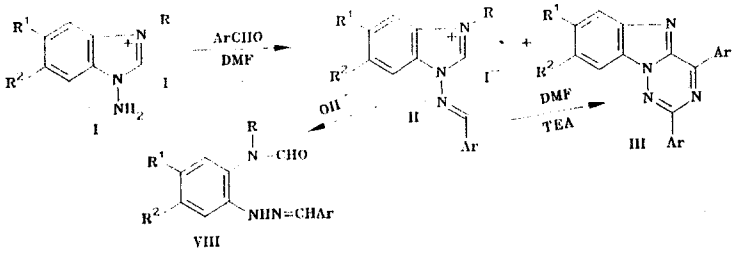
TABLE 1. 1-Arylideneamino-3-alkylbenzimidazolium Iodides IIa-i

Compound	mp,*°C (dec.)	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	I	N		C	H	I	N	
IIa	195—196	49,4	4,1	34,8	11,7	$C_{15}H_{14}IN_3$	49,6	3,9	35,0	11,6	98
IIb	228—229	48,9	4,3	32,2	10,5	$C_{16}H_{16}IN_3O$	48,9	4,1	32,3	10,7	97
IIc	232—233	51,4	4,9	29,9	10,0	$C_{18}H_{20}IN_3O$	51,3	4,8	30,2	10,0	76
IId†	215—216	50,5	4,3	31,5	14,0	$C_{17}H_{19}IN_4$	50,2	4,7	31,3	13,8	96
IIe	218—219	49,5	4,6	35,0	11,3	$C_{15}H_{16}IN_3$	49,3	4,4	34,8	11,5	85
IIg	191—192	45,6	4,0	34,3	11,2	$C_{14}H_{14}IN_3O$	45,8	3,9	34,6	11,4	82
IIh	233—234	60,0	4,1	27,3	9,1	$C_{23}H_{18}IN_3$	59,7	3,9	27,5	9,1	89
IIi	233—234	52,4	4,4	32,3	10,6	$C_{17}H_{18}IN_3$	52,2	4,6	32,5	10,7	87

*Compounds IIa,e,g,i are crystallized from alcohol, IIb,c from butanol, IId from acetic acid, IIh from DMFA.
†The compound was obtained in glacial acetic acid.



I-III a-d, f-i R = CH_3, e R = C_2H_5; a,b,d-h $R^1 = R^2 = H$, c, i $R^1 = R^2 = CH_3$; a,e,i Ar = C_6H_5, c,c Ar = p-$CH_3OC_6H_4$, d Ar = p-$(CH_3)_2NC_6H_4$, f Ar = p-$NO_2C_6H_4$, g Ar = 5-methylfuryl, h Ar = 10-$C_{14}H_9$.

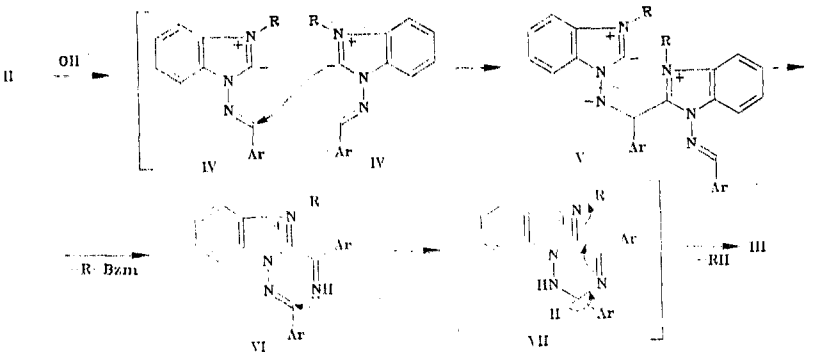
However, experimental verification showed that increase in the amount of the aldehyde introduced into the reaction up to 2 mmoles does not affect the yield of compounds III. When the known aldimine II is heated in DMFA, it gradually transforms into compound III (after 4 h, the yield of, for example, IIIa is 17%), i.e., the second aldehydic fragment necessary for building the molecule of III is formed as the result of direct degradation of aldimine II. Our assumption that the N—N bond is split was confirmed experimentally, when deamination products of aldimines II, 1-alkylbenzimidazoles, were isolated from the reaction mixture.

The high lability of the N—N bond in the 1-aminobenzimidazolium cations was already previously observed during the thermal rearrangment of 1-acylamino-3-alkylbenzimidazolium salts into 1-alkyl-2-acylaminobenzimidazoles [2]. Taking into account the data of the elemental analysis and in analogy with this reaction, the structure of 2,3-diaryl-as-triazino [2,3-a]benzimidazoles could be ascribed to compounds III. However, 2,3-diphenyl-as-triazino [2,3-a]benzimidazole, obtained by an independent method from 1,2-diaminobenzimidazole and benzil [3], differs in its physicochemical characteristics from compound IIIa.

An important structural feature of N-aminobenzimidazolium cations is the high CH-acidity of the meso-carbon atom of the heterocyclic ring. This feature imparts a unique imprint on many reactions of N-aminobenzimidazoles, and has been more than once mentioned in our publications [4, 5]. There is no doubt that specifically in this case, together with the thermal instability of the N—N bond in cations II, this factor plays a decisive role in the annelation of the triazine ring. It can be assumed that the reactive yield IV formed during the deprotonation of the $C_{(2)}$ atom, intermolecularly attacks the polarized C=N bond of the azomethine fragment with the formation of cation V. The cleavage of the N—N bond* in the latter

*If we assume the splitting of the N—N bond in aldimines II and the consequent formation of a benzonitrile "cation," the existence of the latter in the presence of a base, as indicated below, is not very probable.

leads to splitting off of a molecule of 1-alkylbenzimidazole and intermediate VI, which cyclizes into a dihydride derivative VII, and aromatizes due to splitting off of an alkane molecule to form triazinobenzimidazole III



This scheme shows that the reaction should be activated in the presence of a base, favoring the formation of ylide IV, However, on the other hand, it is known [1] that the action of potassium carbonate on azomethine II in a DMFA solution, even at 50°C, causes the opening of the imidazole ring and leads to hydrazones VIII. We found that successful formation of triazinobenzimidazoles III depends on the temperature conditions of the reaction and the basicity of the medium. Thus, in a boiling DMFA, but in the presence of the less basic triethylamine, the yield of compounds III increases twofold, while hydrazones VIII are almost not formed. However, in DMFA at 50°C, or in a boiling alcohol, even triethylamine shifts the reaction totally in the direction of hydrazones VIII. Thus, DMFA plays in the reaction its conventional role of a high boiling solvent with low solvating power.

In conclusion, we should note that the yield of triazinobenzimidazoles III increases from 20 to 60% with increase in the acceptor properties of the substituent in the phenyl ring of the aldehyde, which can readily be explained by the proposed reaction scheme.

EXPERIMENTAL

The IR spectra were run on a UR-10 spectrophotometer, and PMR spectra of a Tesla BS487 spectrometer, with HMDS used as an internal standard. The mass spectra were measured on a Varian MAT-311A mass spectrometer with a direct introduction of the sample into the ionic source, accelerating voltage of 3 kV, cathode emission current 300 μA, ionizing voltage 70 eV.

General Method for the Preparation of 1-Arylideneamino-3-alkylbenzimidazolium Iodides (II). Equimolecular amounts of 1-amino-3-alkylbenzimidazolium iodides (I) and the corresponding aldehydes in alcohol are boiled for 2-3 h. Salts II which separate on cooling are separated and washed with alcohol. The physicochemical constants of iodides II are given in Table 1.

2,4-Diphenyl-as-triazino[1,6-a]benzimidazole (IIIa). A solution of 1.8 g (5 mmoles) of salt IIa in 7 ml of DMFA is boiled for 4 h. The solvent is distilled in vacuo, the residue is treated with 20 ml of chloroform, and 0.3 g of 1-methylbenzimidazole hydroiodide is filtered. The latter is treated with a 22% solution of NH_4OH, and extracted by chloroform, passed through a column with Al_2O_3 (chloroform) to yield 0.15 g (42%) of 1 methylbenzimidazole, mp 60-62°Cfrom hexane). According to data in [6], mp 60-61°C. The chloroform extract is passed through a column with Al_2O_3 (eluent benzene) to yield 0.1 g (17%) of compound IIIa. Yellow-green needles, mp 233-234°C (from butanol). PMR spectrum ($CDCl_3$): 7.42 (8H, m, aromatic protons); 8.1 (2H, m, aromatic protons); 8.33 (2H, q, 4-2'H), and 9.0 ppm (2H, q, 2-2'H). Found: C 78.2; H 4.1; N 17.5%. M^+ 322. $C_{21}H_{14}N_4$. Calculated: C 78.3; H 4.3; N 17.4%.

A solution of 0.9 g (2.5 mmoles) of iodide IIa and 0.35 ml (2.5 mmoles) of triethylamine (TEA) in 4 ml of DMFA is boiled for 2 h. The solution first becomes red, and the the color gradually clears up. When cool, the precipitate is filtered and washed with alcohol. Yield, 0.15 g (38%) yellow-green needles, mp 233-234°C (from butanol).

A solution of 1.37 g (5.0 mmoles) of 1-amino-3-ethylbenzimidazolium iodide and 0.5 ml (5.0 mmoles) of benzaldehyde in 8 ml of DMFA is boiled for 2.5 h. After cooling, the

yellow precipitate is separated and washed with alcohol. Yield, 0.1 g (17%). Green-yellow needles, mp 233-234°C (from butanol). The product does not depress the melting point of a mixed probe with a sample from experiment A. The filtrate is evaporated in vacuo, and the residue is ground with alcohol. The precipitate of 1-benzylideneamino-3-ethylbenzimidazolium iodide is separated and washed with alcohol. Yield, 0.4 g (22%). Pale-yellow prisms, mp 218-219°C (dec. from alcohol). Found: C 49.1; H 4.7; I 35.0; N 11.6%. $C_{15}H_{16}IN_3$. Calculated: C 49.3; H 4.4; I 34.8; N 11.5%.

2,4-Di(p-methoxyphenyl)-as-triazino[1,6-a]benzimidazole (IIIb). A solution of 1.4 g (5.0 mmoles) of salt Ib and 0.6 ml (5.0 mmoles) of anisaldehyde in 10 ml of DMFA is boiled for 3 h. After cooling, the precipitate is filtered and washed with alcohol. The precipitate (0.5 g) is treated with 30 ml of hot chloroform to yield 0.3 g (15%) of iodide IIb, pale-yellow needles, mp 228-229°C (dec. from butanol). The chloroform extract is passed through a column with Al_2O_3 (chloroform) collecting a yellow fraction. Yield 0.15 g (16%). Yellow-green fibrous crystals, mp 201-202°C (from butanol). PMR spectrum ($CDCl_3$): 3.7 (3H, s, OCH_3), 3.75 (3H, s, OCH_3); 6.82 (2H, d, J = 9.0 Hz, 4-3'H); 6.9 (2H, d, J = 9.0 Hz, 2-3'H); 7.35 (2H, m, aromatic protons); 7.9 (2H, m, aromatic protons); 8.23 (2H, d, J = 9.0 Hz, 4-2'H), and 9.0 ppm (2H, d, J = 9.0 Hz, 2-2'H). Found: c 72.6; H 4.5; N 14.9%. M^+ 382. $C_{23}H_{18}N_4O_2$. Calculated: C 72.3; H 4.7; N 14.7%.

A solution of 0.5 g (1.3 mmoles) of salt IIb in 3 ml of DMFA is boiled for 2 h. When cool, 0.12 g (23%) of the initial salt is filtered, and the filtrate is diluted three times its volume with water. The mixture is extracted by 15 ml of chloroform and the extract is purified chromatographically on Al_2O_3 (eluent chloroform), collecting the first fraction. Yield, 0.05 g (20%). Yellow-green needles, mp 201-202°C (from butanol. No depression of the melting point of a mixed probe with a sample from the preceding experiment is observed.

2,4-Di(p-methoxyphenyl)-7,8-dimethyl-as-triazino[1,6-a]benzimidazole (IIIc). A solution of 1.5 g (3.6 mmoles) of iodide IIc and 0.7 ml (5.0 mmole) of TEA in 5 ml of DMFA is boiled for 2 h, and after cooling, 0.13 g (18%) of compound IIIc is filtered. Yellow prisms, mp 263-264°C (from butanol). PMR spectrum (CF_3COOH): 2.18 [6H, s, 7,8-$(CH_3)_2$]; 3.5 (3H, s, OCH_3), 3.6 (3H, s, OCH_3); 6.58 (2H, d, J = 9.0 Hz, 4-3'H); 6.8 (2H, d, J = 9.0 Hz, 2-3'H); 7.33 (1H, s, 6-H); 7.73 (1H, s, 9-H); 7.8 2H, d, 9.0 Hz, 4-2'H), and 8.0 ppm (2H, d, J = 9.0 Hz, 2-2'H). Found: C 73.4; H 5.3; N 13.6%. M^+ 410. $C_{25}H_{22}N_4O_2$. Calculated: C 73.2; H 5.4; N 13.7%.

The filtrate is diluted with 30 ml of water and extracted by 20 ml of chloroform. The chloroform extract is passed through a column with Al_2O_3 (chloroform), collecting the first fraction. The oily residue after the evaporation of chloroform is dissolved in 10 ml of acetone, and treated with concentrated HCl to pH 1. The precipitate is filtered, washed with acetone, and dissolved in 5 ml of water. The solution is neutralized by a 22% NH_4OH solution, and the colorless precipitate is separated and washed with water. The yield of 1,5,6-trimethylbenzimidazole is 0.07 g (21%). Colorless needles, mp 145-147°C (from heptane). PMR spectrum ($CDCl_3$): 2.60 [6H, s, 5,6-$(CH_3)_2$]; 3.68 (3H, s, N-CH_3); 7.10 (1H, s, 7-H); 7.50 (1H, s, 4-H), and 7.65 ppm (1H, s, 2-H). According to the data in [7], mp 142-143°C.

A solution of 1.5 g (5.0 mmoles) of salt Ic and 0.6 ml (5 mmoles) of anisaldehyde in 4 ml of DMFA is boiled for 5 h. The mixture is cooled, and 0.65 g of a precipitate is filtered. The latter is treated with 20 ml of chloroform, and 0.25 g (12%) of aldimine IIc is separated. Cream-colored needles, mp 228-229°C (dec., from butanol), identical with an authentic sample of IIc. The chloroform extract is passed through a column with Al_2O_3 and eluted with chloroform. From the first fraction, 0.12 g of compound IIIc isolated. After evaporation of DMFA and chromatography of the residue, additional 0.08 g of IIIc are obtained. Overall yield 0.2 g (20%). Yellow prisms, mp 263-264°C (from butanol).

2,4-Di(p-dimethylaminophenyl)-as-triazino[1,6-a]benzimidazole (IIId). A solution of 2.8 g (7 mmoles) of salt IId and 1.0 ml (7.5 mmoles) of TEA in 10 ml of DMFA is boiled for 2 h. After cooling, 0.35 g of orange precipitate is filtered off. Treatment of the filtrate by water gives additional 0.06 g of the material. Overall yield, 0.41 g (29%). Orange prisms, mp 225-226°C (from a mixture of butanol with DMFA). PMR spectrum (CF_3COOH): 3.18 [12H, s, 2 $N(CH_3)_2$], 7.62 (4H, m, aromatic protons), 8.2 (4H, d, J = 8.0 Hz, 2,4-3'H), 8.5 ppm (4H, d, J = 8.0 Hz, 2,4-2'H). Found: C 73.5; H 5.9% N 20.8%. $C_{25}H_{24}N_6$. Calculated: C 73.5; H 5.9; N 20.6%.

2,4-Di(p-nitrophenyl)-as-triazino[1-6-a]benzimidazole (IIIf). A mixture of 2.75 g (10 mmoles) of salt Ia and 1.51 g (10 mmoles) of p-nitrobenzaldehyde in 10 ml of DMFA is boiled for 2 h. The precipitate that separated after cooling, is filtered and washed with alcohol. Yield, 1.2 g (60%) Bright-yellow crystals, mp > 300°C (from DMFA). Found: C 61.4; H 3.1; N 20.3%. $C_{21}H_{12}N_6O_4$. Calculated: C 61.2; H 2.9; N 20.4%.

2,4-Di(5-methylfuryl)-as-triazino[1,6-a]benzimidazole (IIIg). A solution of 0.75 g (2 mmoles) of salt IIg and 0.35 ml (2.5 mmoles) of TEA in 3 ml of DMFA is boiled for 2 h. After diluting the mixture with water, the product is extracted by 30 ml of benzene, and then purified chromatographically on Al_2O_3 (eluent benzene). Yield, 0.2 g (60%). Orange crystals, mp 216-217°C (from butanol). Found: C 68.9% H 4.3; N 16.9%. $C_{19}H_{14}N_4O_2$. Calculated: C 69.1; H 4.2; N 17.0%.

2,4-Di(10-anthracenyl)-as-triazino[1,6-a]benzimidazole (IIIh). A solution of 1.15 g (2.5 mmole) of iodide IIh and 0.35 ml (2.5 mmoles) of TEA in 4 ml of DMFA is boiled for 5 h. After cooling, the solution is diluted twice its volume with water, and the precipitate that separates is filtered. Yield, 0.4 g (61%). The product is purified on a column with Al_2O_3 (chloroform, collecting the first fraction. Orange prisms, mp > 310°C (from aqueous DMFA). Found: C 85.2; H 4.4; N 10.7%. $C_{37}H_{22}N_4$. Calculated: C 85.1; H 4.2; N 10.7.

2,4-Diphenyl-7,8-dimethyl-as-triazino[1,6-a]benzimidazole (IIIi). A. A solution of 1.6 g (4 mmoles) of salt IIi and 0.7 ml (5 mmoles) of TEA in 8 ml of DMFA is boiled for 2 h. When cool, 0.25 g (30%) of compound IIIi is filtered. Bright-yellow needles, mp 235-236°C (from butanol). Found: C 78.7; H 5.0; N 15.8% M^+ 350. $C_{23}H_{18}N_4$. Calculated: C 78.9; H 5.1; N 16.0%.

The filtrate is diluted with water (30 ml) and extracted with chloroform to yield 0.15 g (44%) of 1,5,6-trimethylbenzimidazole.

B. A solution of 1.5 g (5 mmoles) of salt Ic and 0.5 ml (0.5 mmoles) of benzaldehyde in 3 ml of DMFA is boiled for 3 h. When cool, 0.65 g of a material is filtered, which is treated with 15 ml of chloroform to yield 0.3 g (15%) of salt IIi, mp 231-232°C (dec. from alcohol). No depression of a melting point of a mixed probe with an authentic sample was observed. The chloroform extract is passed through a column with Al_2O_3 (chloroform), and, first, a yellow fraction — 0.2 g (20%) of compound IIIa — is eluted. Bright-yellow needles, mp 235-236°C (from butanol). Further elution with chloroform gives 0.07 g (17%) of 1,5,6-trimethylbenzimidazole. Weakly rose needles, mp 146-147°C (from heptane).

Benzylidene[o-(N,N-methyl, formyl)]aminophenylhydrazone (VIIIa). A. A mixture of 0.9 g (2.5 mmoles) of salt IIa and 0.35 ml (2.5 mmoles) of TEA in 4 ml of DMFA is stirred for 2 h at 50°C. When cool, the solution is diluted thrice its volume with water, and the precipitate that forms is separated and purified chromatographically on a column with Al_2O_3 (chloroform). Yield 0.4 g (63%). Pale-rose prisms, mp 178-179°C (dec. from butanol), which corresponds to the data in [1].

B. A mixture of 0.9 g (2.5 mmoles) of salt IIa and 0.35 g (2.5 mmoles) of potassium carbonate in 4 ml of DMFA is boiled for 2 h. The solution becomes first red, and after 50 min, the color clears up. After a threefold dilution with water, the material is extracted by 20 ml of chloroform and purified as in the preceding experiment. Yield, 0.25 g (40%), mp 178-179°C (from alcohol).

C. A solution of 0.55 g (2 mmoles) of salt IIa and 0.28 g (2 mmoles) of TEA in 8 ml of alcohol is boiled for 6 h. After cooling, the precipitate formed is separated and washed with alcohol. Yield, 0.3 g (60%). Weakly rose prisms, mp 177-178°C (from alcohol). No depression of melting point of a mixed probe with an authentic sample is observed.

p-Methoxybenzylidene[o-(N,N-methyl, formyl)]amino-4,5-dimethylphenylhydrazone (VIIIc). A suspension of 0.42 g (1 mmole) of salt IIc and 0.2g (1.5 mmoles) of potassium carbonate in 10 ml of water is stirred for 5 min at 80°C, whereby the form of the precipitate changes; it is filtered and washed with water. Yield, 0.25 g (80%). Grayish needles, mp 175-176°C (from alcohol). IR spectrum ($CHCl_3$): 1670 (C=O), 3260 cm^{-1} (N—H). Found: C 69.8; H 6.8; N 13.7%. $C_{18}H_{21}N_3O_2$. Calculated: C 69.5; H 6.8; N 13.5%.

Benzylidene[o-N,N-methyl,formyl)]amino-4,5-dimethylphenylhydrazone (VIIIi). A suspension of 1.0 g (2.5 mmoles) of salt IIi and 0.5 g (3.6 mmoles) of potassium carbonate in 10 ml of water is stirred at 80°C for 10 min. When cool, the precipitate is filtered and washed with water. Yield, 0.7 g (quantitative). The material is purified chromatographically on a column

with Al_2O_3, collecting the first fraction. Weakly rose prisms, mp 174-175°C (from alcohol). Found: C 72.4; H 7.1; N 15.0%. $C_{17}H_9N_3O$. Calculated: C 72.6; H 6.8; N 14.9%.

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FORMATION OF 4,5-DIHYDRO-1,2,4-TRIAZOLES DURING REARRANGEMENT OF O-ACETYL DERIVATIVES OF 1,2-HYDROXYLAMINOHYDRAZONES AND THIOSEMICARBAZONES

N. V. Belova, L. B. Volodarskii, and A. Ya. Tikhonov

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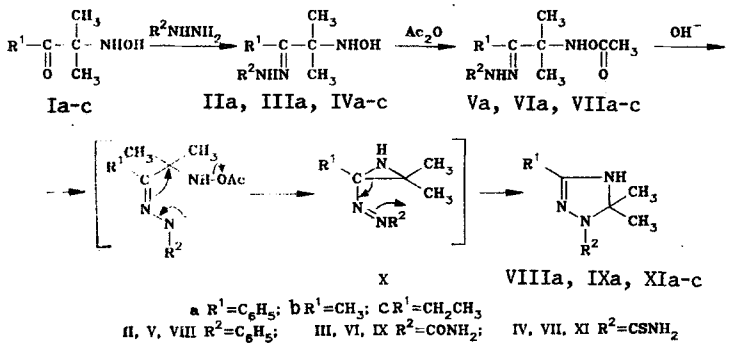
Acylation of phenylhydrazone, semicarbazone, and thiosemicarbazones of 1,2-hydroxylamino-ketones containing a hydroxylamine group at the tertiary carbon atom, by acetic anhydride, leads to products of O-acylation at the hydroxylamine group, which in alkali medium rearrange to form 4,5-dihydro-1,2,4-triazoles.

It has already been discovered that oximes of 1,2-(O-acylhydroxylamino)ketones, containing an acyloxyamino group at the tertiary carbon atom, split off a molecule of a carboxylic acid by the action of alkali and rearrange into 4,5-dihydro-1,2,4-oxadiazoles [1].

In the present work, we have studied the action of alkali on the hydrazones of the same 1,2-hydroxylamino-ketones to verify the generality of the rearrangement discovered. From the 1,2-hydroxylamino-ketones Ia-c, we synthesized a phenylhydrazone IIa, semicarbazone IIIa, and thiosemicarbazones (IVa-c). Their acylation by acetic anhydride smoothly leads to O-acetyl derivatives Va, VIa, and VIIa-c, respectively.



Ia-c IIa, IIIa, IVa-c Va, VIa, VIIa-c

X VIIIa, IXa, XIa-c

a $R^1=C_6H_5$; b $R^1=CH_3$; c $R^1=CH_2CH_3$

II, V, VIII $R^2=C_6H_5$; III, VI, IX $R^2=CONH_2$; IV, VII, XI $R^2=CSNH_2$

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090.

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