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%.

LITERATURE CITED

1. Y. Tamura, H. Hayashi, Y. Nishimura, and M. Ikeda, J. Heterocycl. Chem., 12, 225 (1975).
2. Y. Tamura, H. Hayashi, J. Minamikawa, and M. Ikeda, J. Heterocycl. Chem., 11, 781 (1974).
3. A. V. Zeiger and M. M. Joullie, J. Org. Chem., 42, 542 (1977).
4. V. V. Kuz'menko, V. N. Komissarov, and A. M. Simonov, Khim. Geterotsikl. Soedin., No. 11, 1497 (1981).
5. V. V. Kuz'menko, T. A. Kuz'menko, and A. M. Simonov, Khim. Geterotsikl. Soedin., No. 2, 256 (1983).
6. A. F. Pozharskii and A. M. Simonov, Zh. Obshch. Khim., 33, 179 (1963).
7. A. M. Simonov, A. F. Pozharskii, and V. M. Marianovskii, Indian J. Chem., 5, 81 (1967).

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

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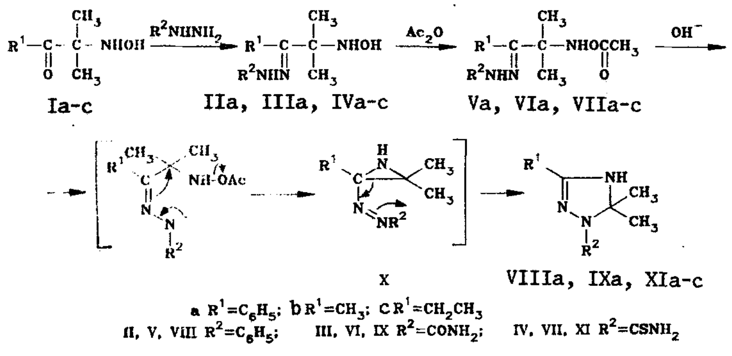
UDC 547.288.3.4'792:543.422

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 $R^2=CSNH_2$

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TABLE 1. Spectral Characteristics of Compounds Synthesized III-IX, XI

Compound	IR spectrum (in KBr), cm^{-1}	UV spectrum λ_{max}, nm (log ε)	PMR spectrum, ppm
IIIa	1685 (C=O)	234 sh(4,09)	1,22 (6H, s, CH_3); 7,1—7,6 (5H, m, C_6H_5)
IVa	—	234 sh(4,10), 278 (4,40)	1,15 (6H, s, CH_3); 7,1—7,4, 7,4—7,6 [6H, m, C_6H_5 NH(OH)]; 5,70, 7,80, 8,00, 8,45 (NH_2, NH, OH)
IVc	—	274 (4,53)	0,99 (3H, t, J=7,5 Гц, CH_3); 1,14 (6H, s, CH_3), 2,47 (2H, q, J=7,5 Гц, CH_2); 6,94, 7,57, 8,13, 9,76 (NH_2, NH, OH)
Va	1730 (C=O)	271 (4,22), 295 (4,03)	1,25 (6H, s, CH_3); 1,97 (3H, s, CH_3); 7,0—7,5 (10H, m, C_6H_5); 7,74, 7,93 (NH)
VIa	1670, 1700, 1750 (C=O)	225 sh(4,15)	1,27 (6H, s, CH_3); 2,04 (3H, s, CH_3); 7,1—7,3, 7,4—7,6 (5H, m, C_6H_5)
VIIa	1730 (C=O)	236 (4,08), 279 (4,36)	1,29 (6H, s, CH_3); 2,04 (3H, s, CH_3); 7,1—7,3, 7,4—7,6 (5H, m, C_6H_5)
VIIb	1730 (C=O)	232 (4,00), 273 (4,46)	1,27 (3H, s, CH_3); 2,01 (3H, s, CH_3); 2,07 (3H, s, CH_3); 7,84, 8,34, 10,34 (NH_2, NH)
VIIc	1720 (C=O)	233 sh (3,98), 276 (4,44)	0,96 (3H, t, J=7,5 Гц, CH_3); 1,24 (6H, s, CH_3); 1,98 (3H, s, CH_3); 2,51 (2H, q, J=7,5 Hz, CH_2); 7,54, 8,04, 8,20, 9,90 (NH_2, NH)
VIIIa	3330 (NH)	228 (4,29), 263 sh(3,94), 350 (4,08)	1,57 (6H, s, 5,5—CH_3); 7,2—7,5, 7,6—7,8 (10H, m, 1,3-C_6H_5)
IXa	1660 (C=O), 3200, 3380, 3520 (NH_2, NH)	232 (4,24), 324 (3,90)	1,61 (6H, s, 5,5-CH_3); 6,01 (NH_2); 7,4—7,6, 7,6—7,9 (6H, m, 3-C_6H_5 и NH)
XIa	3140, 3260, 3380, 3440 (NH_2, NH)	235 (4,23), 342 (4,11)	1,94 (6H, s, CH_3); 7,4—7,6, 7,7—8,0 (5H, m, C_6H_5); 7,30, 8,12, 8,32 (NH_2, NH)
XIb	3160, 3270, 3380 (NH_2, NH)	238 (4,06), 297 (4,18)	1,90 (9H, s, 3,5,5-CH_3); 7,17, 7,96 (NH_2, NH)
XIc	3170, 3280, 3390 (NH_2, NH)	237 (4,07), 295 (4,18)	1,09 (3H, t, J=7,5 Hz, 3-CH_2CH_3); 2,19 (2H, q, J=7,5 Hz, 3-CH_2CH_3); 6,97, 7,64 (NH_2, NH)

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*UV spectrum of IIa, λ_{max}, nm (log ε): 269 (4.26), 294 (4.00).
†The PMR spectra of IVa,c, VIIb,c, IXa, XIa-c were recorded in $(CD_3)_2SO$, of IIIa, VIa, VIIa in CD_3OD, of VIIIa in $CDCl_3$.

TABLE 2. Data of ^{13}C NMR Spectra of Compounds III, IV, VII-IX, X (in DMSO)

Compound	R^1	C=N	$-\overset{\vert}{\underset{\vert}{C}}-$	CH_3	R^2
IIIa	127,8, 129,1, 132,0	154,8 or 156,0	61,4	23,7	154,8 or 156,0
IVa	127,6, 129,3, 131,5	158,0	61,6	23,8	177,8
VIIa*	127,5, 129,4, 131,2	155,7	61,7	24,0	178,1
VIIIa (in acetone)	128,9, 129,1, 129,7	148,7	83,1	27,1	116,9, 120,1, 125,8, 145,8
IXa	125,9, 127,6, 128,4, 130,0	148,7 or 154,9	79,3	27,0	148,7 or 154,9
XIa	126,4, 128,4, 130,7	150,0	81,9	27,1	172,5
XIb	11,4	150,8	80,9	26,8	171,5
XIc	10,5, 19,1	155,2	80,9	26,8	171,8

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*The signals for the acetoxyl group are observed at 19.1 (CH_3) and 169.9 ppm (C=O).

TABLE 3. Characteristics of Compounds Synthesized II-IX, XI

Compound	mp,* °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	N	S		C	H	N	S	
IIa	120—122	71,8	7,2	15,8	—	$C_{16}H_{19}N_3O$	71,4	7,1	15,6	—	63
IIIa	145—146	55,5	7,2	23,2	—	$C_{11}H_{16}N_4O_2$	55,9	6,8	23,7	—	70
IVa	201—203	52,2	6,4	22,1	12,4	$C_{11}H_{16}N_4OS$	52,4	6,5	22,2	12,7	95
IVc	127—129	41,6	8,6	27,0	15,4	$C_7H_{16}N_4OS$	41,2	8,0	27,4	15,7	63
Va	95—97	69,1	7,0	13,7	—	$C_{18}H_{21}N_3O_2$	69,4	6,8	13,5	—	70
VIa	108—109	55,8	6,5	19,9	—	$C_{13}H_{18}N_4O_3$	56,1	6,5	20,1	—	71
VIIa	168—170	52,9	6,1	19,2	10,6	$C_{13}H_{18}N_4O_2S$	53,0	6,1	19,1	10,9	98
VIIb	126—128	41,1	6,5	23,9	13,6	$C_8H_{16}N_4O_2S$	41,4	6,9	24,1	13,8	78
VIIc	120—122	43,3	7,5	22,5	13,1	$C_9H_{18}N_4O_2S$	43,9	7,4	22,8	13,0	76
VIIIa	113—115	76,4	6,6	16,5	—	$C_{16}H_{17}N_3$	76,5	6,8	16,7	—	67
IXa	162—164	60,6	6,5	25,7	—	$C_{11}H_{14}N_4O$	60,5	6,5	25,7	—	46
XIa	134—135	56,4	6,1	23,7	13,6	$C_{11}H_{14}N_4S$	56,4	6,0	23,9	13,7	59
XIb	186—188	42,0	7,2	32,5	18,1	$C_6H_{12}N_4S$	41,8	7,0	32,6	18,6	30
XIc	149—151	44,7	7,6	30,1	17,1	$C_7H_{14}N_4S$	45,1	7,5	30,1	17,2	71

*Compound Ia was crystallized from aqueous alcohol; IIIa and IVa from alcohol; IVc and XIa,c from ethyl acetate, VIIIa from hexane; Va, VIa, and VIIa-c by reprecipitation from chloroform by hexane; IXa and XIb were purified chromatographically.

The presence of a stretching vibration band of the C=O bond in the 1720-1750 cm^{-1} region in the IR spectra of compounds Va, VIa, and VIa-c (Table 1) correlates with the fact that they are products of acylation at the oxygen atom of the hydroxylamino group (cf. [1].

When the solution of O-acetyl derivative of phenylhydrazone Va in dioxane was treated by aqueous sodium hydroxide, a solid crystalline product VIIIa was isolated in a ~70% yield, with an elemental composition (Table 3) corresponding to a split off of a molecule of acetic acid from Va. In its IR spectrum in CCl$_4$, there is a band at 3380 cm^{-1} (NH), while the UV spectrum is similar to the UV spectrum of the known 5,5-dimethyl-1,3,4-triphenyl-4,5-dihydro-1,2,4-triazole [2]. These data, and also the signal at 83.1 ppm observed in the ^{13}C NMR spectrum (Table 2), characteristic for 4,5-dihydro-1,2,4-triazoles [3], permit us to ascribe the structure of 5,5-dimethyl-1,3-diphenyl-4,5-dihydro-1,2,4-triazole to compound VIIIa.

Under similar conditions, the O-acetyl derivative of semicarbazone VIa converts into 5,5-dimethyl-1-carbamoyl-3-phenyl-4,5-dihydro-1,2,4-triazole (IXa) (Table 1-3).

In a similar treatment of solutions of O-acetyl derivatives of thiosemicarbazones VIIa-c, compounds XIa-c were isolated (Tables 1-3). In the IR spectrum of compound XIa (in CCl$_4$), in addition to the band at 3380 cm^{-1}, two bands are observed at 3240 and 3520 cm^{-1}, assignable to the stretching vibrations of the N—H bonds. In the IR spectra of compounds XIa-c (in KBr), an intense absorption band is observed in the 1340-1360 cm^{-1} region, which in its position is similar to the C=S group vibration band in thioamides, thiosemicarbazides [4, 5], and triazolinetriones [5], and is absent in the IR spectra of 4,5-dihydro-1,2,4-triazoles VIIIa and IXa.

To explain the rearrangement, it can be assumed that initially compound X, containing an aziridine ring is formed (cf. [6]), with subsequent cleavage of the C^2—C^3 bond and the formation of the R^{2}N—C^3 bond.

It should be noted that the action of alkali on compounds VIIa-c leads in practically all cases to the formation of deacylation products, namely, thiosemicarbazones IVa-c. According to literature data, 4,5-dihydro-1,2,4-triazoles are formed during the condensation of amidrazones with aldehydes and ketones [3, 7], or by cycloaddition of nitrilimines to imine derivatives [8]. No information is available on 4,5-dihydro-1,2,4-triazoles Xa and XIa-c, containing a carbamoyl or a thiocarbamoyl group as substituents.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in KBr tablets or in a CCl$_4$ solution, and the PMR spectra on a Varian A-56/60A spectrometer (60 MHz), using HMDS as internal standard. The ^{13}C NMR spectra were run on Bruker HX-90 (22.63 MHz) and Bruker WP-

200SY (50.3 MHz) spectrometers for 10-15% solutions. The UV spectra were run in alcohol on a Specord UV-Vis spectrophotometer. The course of the reactions was controlled on Silufol UV-254 plates, with development by UV light and iodine vapors.

The spectral characteristics of the compounds synthesized are given in Tables 1 and 2, and the physicochemical characteristics in Table 3.

Phenylhydrazone of 2-Hydroxyamino-2-methyl-1-phenyl-1-propanone (IIa). A 6.6 g (35 mmole) portion of compound Ia [9] in 60 ml of alcohol is added to a solution prepared by adding 10 ml of 50% acetic acid to a mixture of 15 ml (153 mmoles) of phenylhydrazine and 132 ml of water. The reaction mixture is stirred to a complete dissolution of Ia, and then for another 2 h. The precipitate is filtered, washed with water, and dried. Yield, 6.0 g of hydrazone IIa.

Semicarbazone of 2-hydroxyamino-2-methyl-1-phenyl-1-propanone (IIIa). A mixture of 1.9 g (25 mmoles) of semicarbazide and 5.4 g (25 mmoles) of Ia hydrochloride in 40 ml of ethanol is boiled for 2 h. The alcohol is evaporated, the residue is dissolved in 30 ml of water, 1.7 g (12.5 mmoles) of potassium carbonate are added, and the mixture is extracted by ethyl acetate. The ethyl acetate solution is dried over magnesium sulfate, and evaporated. Yield, 4.8 g of semicarbazone IIIa.

Thiosemicarbazone of 2-hydroxyamino-2-methyl-3-pentanone (IVc) is obtained in a similar way from Ic hydrochloride [10].

Thiosemicarbazone of 3-hydroxyamino-3-methyl-2-butanone (IVb) was obtained according to [11].

Thiosemicarbazone of 2-Hydroxyamino-2-methyl-1-phenyl-1-propanone (IVa). A mixture of 5.2 g (33 mmoles) of thiosemicarbazide and 7.1 g (33 mmoles) of Ia hydrochloride in 50 ml of ethanol is boiled for 1 h. The alcohol is evaporated, and the residue is dissolved in 50 ml of water and 2.3 g (16.5 mmoles) of potassium carbonate are added. The precipitate is filtered and dried. Yield, 7.9 g of thiosemicarbazone IVa.

Phenylhydrazone of 2-acetoxyamino-2-methyl-1-phenyl-1-propanone (Va). A 0.4 ml (3.9 mmole) portion of acetic anhydride is added to a suspension of 1.0 g (3.7 mmoles) of IIa in 20 ml of dry ether. The mixture is held up to the disappearance of phenylhydrazone IIa (TLC control). Ether is evaporated, and the residue is crystallized by grinding in petroleum ether and filtered. Yield, 0.8 g of the acetyl derivative of Va.

Semicarbazone of 2-acetoxyamino-2-methyl-1-phenyl-1-propanone (VIa) is obtained in a similar way.

Thiosemicarbazone of 3-acetoxyamino-3-methyl-2-butanone (VIIb). A 0.5 ml (5 mmole) portion of acetic anhydride is added, with stirring, to a suspension of 0.9 g (5 mmoles) of IVb in 25 ml of dry ether. After 4 h the precipitate is filtered and washed with ether. Yield, 0.9 g of VIIb.

Thiosemicarbazones of 2-acetoxyamino-2-methyl-1-phenyl-1-propanone and 2-acetoxyamino-2-methyl-3-pentanone (VIIc) are obtained in a similar way.

5,5-Dimethyl-1,3-diphenyl-4,5-dihydro-1,2,4-triazole (VIIIa). An 8 ml portion of 1 N NaOH is added, with stirring, to a solution of 2.5 g (8 mmoles) of Va in 25 ml of dioxane and the reaction mixture is held up to the disappearance of the initial Va (TLC control). Dioxane is evaporated, 30 ml of water are added, and the mixture is extracted by chloroform. The extract is dried over magnesium sulfate, evaporated, and the residue is crystallized by grinding in hexane. Yield, 1.2 g.

5,5-Dimethyl-1-thiocarbamoyl-3-ethyl-4,5-dihydro-1,2,4-triazole (XIc) is obtained in a similar way.

5,5-Dimethyl-1-thiocarbamoyl-3-phenyl-4,5-dihydro-1,2,4-triazole (XIa). A 7.5 ml portion of 1 N NaOH is added, with stirring, to a solution of 2.2 g (7.5 mmoles) of VIIa in 22 ml of dioxane, and the mixture is held up to the disappearance of VIIa (TLC control). Dioxane is evaporated and 30 ml of water and chloroform were added. The precipitate of thiosemicarbazone IVa, separating at the phase interface of chloroform and water, is filtered. Yield, 0.34 g of IVa. The chloroform solution is separated, and the aqueous layer is extracted with chloroform. The combined chloroform solution is dried over magnesium sulfate, and evaporated. Chromatography of the residue on a column with silica gel (eluent chloroform) gives 0.9 g of XIa.

Compounds IXa and XIb are obtained in a similar way.

LITERATURE CITED

1. A. Ya. Tikhonov, N. V. Belova, L. B. Volodarskii, and Yu. V. Gatilov, Zh. Org. Khim., 21, 196 (1985).
2. R. Huisgen, R. Grashey, R. Kunz, G. Wallbillich, and E. Aufderhaar, Chem. Ber., 98, 2174 (1965).
3. K. N. Zelenin, V. A. Khrustalev, and V. P. Sergutina, Zh. Org. Khim., 16, 942 (1980).
4. P. W. Sadler, J. Chem. Soc., No. 3, 957 (1961).
5. V. I. Kelarev, G. A. Shvekhgeimer, and L. F. Lunin, Khim. Geterotsikl. Soedin., No. 9, 1271 (1984).
6. D. A. Clark, C. A. Bunnel, and P. L. Fuchs, J. Amer. Chem. Soc., 100, 7777 (1978).
7. B. G. Bassar and F. V. Mathis, C. R. Acad. Sci., C, 258, 6470 (1964).
8. J. B. Polya, in: Comprehensive Heterocyclic Chemistry, Vol. 5, A. R. Katritzky and C. W Rees, editors, Pergamon Press, Oxford—New York—Toronto—Sydney—Paris—Frankfurt (1984), p. 769.
9. L. B. Volodarskii and T. K. Sevastyanova, Zh. Org. Khim., 7, 1687 (1971).
10. I. A. Grigor'ev, A. G. Druganov, and L. B. Volodarskii, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 9, 131 (1976).
11. V. N. Kirichenko, S. V. Larionov, E. G. Boguslavskii, V. I. Lavrent'eva, and L. B. Volodarskii, Zh. Neorg. Khim., 31, 835 (1986).

QUANTUM-CHEMICAL INTERPRETATION OF RECYCLIZATION REACTIONS.

10.* PHOTOISOMERIZATION OF SIX-MEMBERED HETEROCYCLES

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UDC 541.141:539.196:547.72'77'78

Singlet photoisomerizations of a number of six-membered heterocycles have been described on the basis of the index approach in the framework of the coupled variant of perturbation theory for a one-electron transition density matrix in the Pariser—Parr—Pople method.

In the preceding investigations of this series we developed a quantum-chemical approach to the description of the recyclization reactions of molecules with conjugate bonds on the basis of the coupled variant of perturbation theory. In the case of dark reactions, the orders of the bonds between not directly bonded atoms of the molecule P_{ik} serve as the reactivity indices. In the case of photochemical reactions of the X type in Dougherty's terminology [2], we obtained [3] more complicated expressions for the reactivity indices $K_{ik}^{S,T}$, to which the main contribution is made by the changes in the long-range bond orders upon excitation of the molecule. This approach was tested in the example of the photochemical contraction reaction of the furan ring [3] and a number of photoisomerizations of five-membered heterocycles [1]. In the present work it was extended to the case of singlet photoisomerizations of six-membered heterocycles.

1. As follows from Table 1, which presents the reactivity indices of singlet photoisomerization of azines, the excitation of the pyridine molecule (I) results in a sharp increase in the role of the nonclassical structures, particularly of Dewar azabenzene and azaprismane. This is manifested by the presence of large positive values for $K_{2,5}^S$ and $K_{1,4}^S$. At the same time, the sum of these parameters in the first singlet state with the corresponding P_{ik} is close to zero. This is primarily an indication of the possible strong influence of the substituents and even of the solvent on the nature of the transition state, and, in the final

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*For Communication 9, see [1].

Institute of Physical Organic Chemistry and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk 340114. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 357-363, March, 1986. Original article submitted December 14, 1983; revision submitted December 28, 1984.

0009-3122/86/2203-0291$12.50