at temperatures lower than 40°C. The residue was recrystallized from ether (IIIe, f; Va, b, f, g) or purified chromatographically on a Silpearl silica gel column using hexane—ethyl acetate (gradient from 2:1 to 1:4) (IIId, g; Vc, d, e). Physical constants and yields are summarized in Tables 1 and 2.

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PREPARATION OF 2,3,4,5-TETRAHYDRO-1,2,4,TRIAZINE-3-ONES

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The reaction of 3-(2-oxoalkyl)-2-benzoxazolones with hydrazine leads to the formation of the corresponding 2,3,4,5-tetrahydro-1,2,4-triazine-3-ones in good yield.

It was shown earlier, in a study of the reaction of 3-(2-oxoalkyl)-2-benzoxazolones (I) with hydrazine hydrate, that, depending on the reaction conditions, hydrazones, azines, or 2,3,4,5-tetrahydro-1,2,3-triazine-3-ones (II) [1] are obtained, the latter, according to the literature, having a wide spectrum of biological activity: they exhibit herbicidal activity [2], strengthen the action of the heart and have anti-hypertension properties [3, 4]. There has in recent years been an increasing interest in the synthesis of compounds of this class [5-8]. The object of the present study was to develop methods for the preparation of 1,2,4-triazine-3-ones II based on 3-(2-oxoalkyl)-2-benzoxazolones (I).

The initial oxoalkylbenzoxazolones I were prepared by alkylation of the corresponding 2-(3H)-benzoxazolones with isomeric bromobutane-2-ones in the presence of solium alkoxide [9]. Two bands due to carbonyl stretching vibrations are observed in the IR spectrum of the ketone I — at 1790-1775 cm^{-1} (amide) and 1760-1730 cm^{-1} (ketone). In addition to other signals, a quadruplet signal from the methine proton at 5.35 ppm (1H) for oxazolones Ia-f and a singlet for the methylene group at 5.1 ppm (2H) for the isomers Ig, h confirmed their structure.

The optimum conditions for the conversion of the benzoxazolones I into 2,3,4,5-tetrahydro,1,2,4-triazine-3-ones (II) proved to be at boiling point in hydrazine hydrate with the

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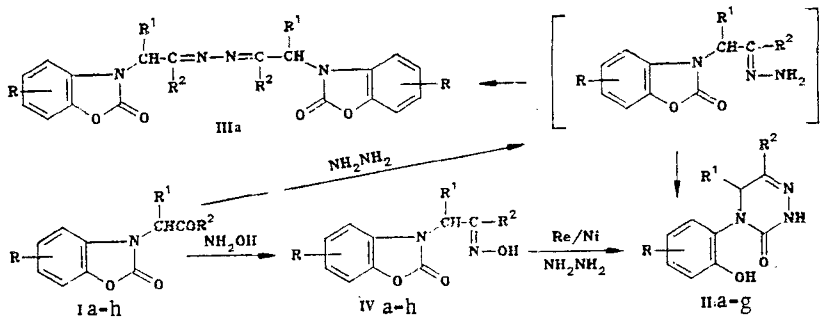
TABLE 1. Properties of Compounds I-IV

Compound	T_{mp}, °C (from EtOH)	Found, N, %	Molecular formula	Calculated N, %	Yield, %
Ia	68—69	6,7	$C_{11}H_{11}NO_3$	6,8	59
Ib	120—121	5,9	$C_{11}H_{10}ClNO_3$	5,8	68
Ic	215—216	9,7	$C_{11}H_{12}N_2O_5S$	9,8	74
Id	105—106	6,0	$C_{11}H_{10}ClNO_3$	5,8	73
Ie	91—92	5,0	$C_{11}H_{10}BrNO_3$	4,9	80
If	188—189	9,8	$C_{11}H_{12}N_2O_5S$	9,8	78
Ig	156—157	5,8	$C_{11}H_{10}ClNO_3$	5,8	35
Ih	160—161	4,9	$C_{11}H_{10}BrNO_3$	4,9	20
IIa	241—242	19,0	$C_{11}H_{13}N_3O_2$	19,2	80
IIb	198—199	16,4	$C_{11}H_{12}ClN_3O_2$	16,6	87
IIc	303—304	18,1	$C_{11}H_{14}N_4O_4S$	18,1	79
IId	217—218	16,5	$C_{11}H_{12}ClN_3O_2$	16,6	62
IIe	223—224	14,3	$C_{11}H_{12}BrN_3O_2$	14,1	88
IIf	238—239	18,2	$C_{11}H_{14}N_4O_4S$	18,1	71
IIg	171—172	16,4	$C_{11}H_{12}ClN_3O_2$	16,6	73
IIIa	148—149	13,8	$C_{22}H_{22}N_4O_4$	13,8	76
IVa	107—108	12,6	$C_{11}H_{12}N_2O_3$	12,7	67
IVb	176—177	10,9	$C_{11}H_{11}ClN_2O_3$	11,0	74
IVd	119—120	10,9	$C_{11}H_{11}ClN_2O_3$	11,0	48
IVe	146—147	9,2	$C_{11}H_{11}BrN_2O_3$	9,4	69
IVg	202—203	10,8	$C_{11}H_{11}ClN_2O_3$	11,0	55
IVh	164—165	9,3	$C_{11}H_{11}BrN_2O_3$	9,4	68

ratio of ketone I to hydrazine hydrate = 1:3. If a ratio around 1:1 were used, the main product was the azine [1].



I—IV a R=H, b R=5-Cl, c R=5-SO_2NH_2, d, g R=6-Cl, e, h R=6-Br, f R=6-SO_2NH_2;
a—e $R^1=R^2=CH_3$, f — h $R^1=H$, $R^2=C_2H_5$

In the proton NMR spectrum of compound IIe there is a singlet at 10.45 ppm corresponding to the imino group and a singlet at 10.00 ppm from the hydroxyl proton. These same groups also appear in the IR spectrum (3260 cm^{-1}).

It was found that the triazines II can also be prepared from the oxoalkylbenzoxazolones I by another route — reaction of their oximes (IV) with hydrazine hydrate in the presence of Re/Ni in a mixture of alcohol and dichloroethane. The oximes IV are readily formed by reacting the ketones I with hydroxylamine hydrochloride in a mixture of alcohol and pyridine at the boiling point.

Attempts to reduce the oximes IV to aminoalkyl derivatives by means of tin, stannous chloride or sodium amalgam led to the detachment of the side chains. Reduction with sodium hydrosulfite in an alkaline medium resulted in the formation of 4-imidazoline-2-ones [10].

EXPERIMENTAL

Infrared spectra were run on a UR-10 instrument in KBr, and NMR spectra of a BS-487-C (80NHz) in DMSO with HMDS as standard. Melting points were obtained by the capillary method and are not corrected.

Characteristics for compounds Ia-h, IIa-g, IIIa, and IVa-h are shown in Table 1.

3-(1-Methyl-2-oxopropyl)-2-benzoxazolones (Ia-e). To a solution of 0.23 g (0.01 mole) sodium in 20 ml ethanol was added, with stirring, 0.01 mole 2-(3H)-benzoxazolone followed by the dropwise addition of 0.01 mole freshly distilled 3-bromobutane-2-one. Stirring was continued for 3 h and the precipitate then filtered off and washed with water.

3-(2-Oxobutyl)-2-benzoxazolones (If, g, h). The method was similar to the foregoing, but on cooling compounds Ig and g were obtained from 2-(3H)-benzoxazolone and 1-bromobutane-2-one. They were recrystallized from ethanol.

Oximes of 3-(2-oxozlkyl)-2-benzoxazolones (IVa-h). A mixture of 0.01 mole ketones I, 0.68 g (0.012 mole) hydroxylamine hydrochloride, 20 ml pyridine and 20 ml ethanol was heated at bp for 4 h, cooled, diluted with water and the precipitate filtered off and washed with water.

1-Methyl-1-(2-benzoxazolone-3-yl)-2-propanone Azine (IIIa). A mixture of 2.05 g (0.01 mole) ketone Ia, 1 ml hydrazine hydrate, and 20 ml ethanol was heated at bp for 2 h, cooled, and the precipitate filtered off and washed with water.

2,3,4,5-Tetrahydro-1,2,4-triazine-3-ones (IIa-g). A mixture of 0.01 mole ketone I, 3 ml hydrazine hydrate, and 20 ml alcohol was heated 6 h at bp, cooled, neutralized with concentrated hydrochloric acid, and the precipitate filtered off and washed with water.

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4- AND 5-HYDROXYLAMINOTHIAZOLIDINE-2-THIONES. ACYLATION, SYNTHESIS, AND STRUCTURAL INVESTIGATION OF NEW 6-THIOXO(OXO) DERIVATIVES OF 4,5-DIHYDRO-6H-1,2,5-THIADIAZINE

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542.951:548.737:541.63

The treatment of 4- and 5-hydroxylaminothiazolidine-2-thiones as well as 5-hydroxylaminothiazolidin-2-one with acetic anhydride or benzoyl chloride is accompanied, as a rule, by the formation of O-acyl derivatives. The 4-(O-acyl) derivatives are thereby either stable to thermal or alkaline treatment, or are converted to 4-iminothiazolidine-2-thione; the 5-(O-acetyl)-hydroxylamines rearrange to 6-thioxo(oxo) derivatives of 4,5-dihydro-6H-1,2,5-thiadiazine.

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