removed from the solutions to be polarographed by means of a stream of purified nitrogen. The DMF was rendered anhydrous by means of fused KOH and was distilled *in vacuo*.

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1,3-OXAZINES.

INTRAMOLECULAR CYCLIZATION OF 1-DIAZO-3-BENZAMIDOPROPAN-2-ONES

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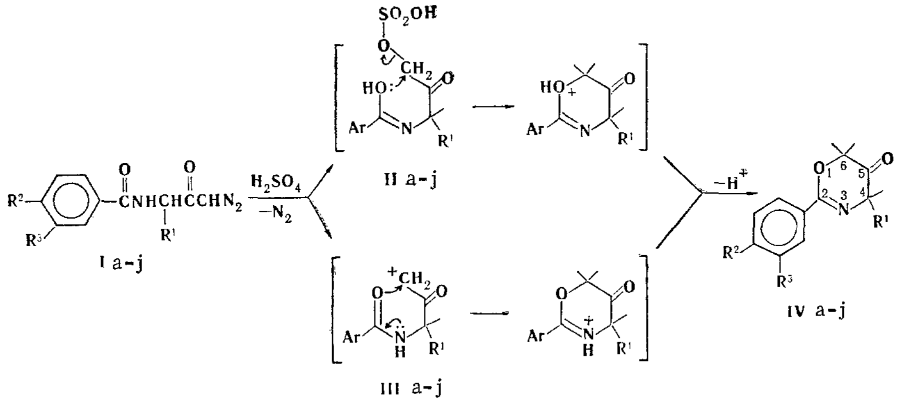
UDC 547.867.2

2-Aryl-5,6-dihydro-4H-1,3-oxazin-5-ones were obtained in the reaction of 1-diazo-3-benzamidopropan-2-ones with acidic agents.

Continuing our research on the intramolecular cyclization reactions of diazo ketones under the influence of acidic agents, which lead to heterocycles [1], we studied the possibility of the formation of the 1,3-oxazine system from 1-diazo-3-benzamidopropan-2-ones (I).

The reaction of Ia-j with concentrated sulfuric acid at room temperature for a few seconds leads to 5,6-dihydro-4H-1,3-oxazin-5-one derivatives (IVa-j). The reaction may proceed both through the carbonium ion (III) generated by protonation of diazo ketones I and through a sulfo ester (II). In both cases the oxygen atom of the benzoyl group undergoes intramolecular alkylation with subsequent splitting out of a proton and the formation of oxazines IVa-j. Alternative ring closing at the nitrogen atom to give an azetidine system does not occur.



I, IV a $R^1=R^2=R^3=H$; b $R^1=R^3=H$, $R^2=CH_3$; c $R^1=R^3=H$, $R^2=Cl$; d $R^1=R^3=H$, $R^2=Br$; e $R^1=R^3=H$, $R^2=NO_2$; f $R^1=H$, $R^2=R^3=OCH_3$; g $R^1=CH_3$, $R^2=R^3=H$; h $R^1=C_2H_5$, $R^2=R^3=H$; i $R^1=CH_2C_6H_5$, $R^2=R^3=H$; j $R^1=CH_2C_6H_5$, $R^2=R^3=OCH_3$

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TABLE 1. Spectral Characteristics of 2-Aryl-5,6-dihydro-4H-1,3-oxazin-5-ones (IV)

Compound	PMR spectrum, δ, ppm; multiplicity, J, Hz (No. of protons	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, (log ε)
IVa	4,22, s (2H); 4,64, s (2H); 7,4—8,0, m (5H)	1700 (C=O), 1640 (C=N), 1580 (C=C)	207 (4,15), 238 (4,08)
IVb	2,39, s (3H); 4,20, s (2H); 4,61, s (2H); 7,2—7,9, m (4H)	1710 (C=O), 1640 (C=N), 1580 (C=C)	208 (4,29), 245 (4,19)
IVc	4,20, s (2H); 4,62, s (2H); 7,35—7,91, q (4H)	1720 (C=O), 1640 (C=N), 1580 (C=C)	208 (4,22), 246 (4,16)
IVd	4,19, s (2H); 4,62, s (2H); 7,54—7,9, q (4H)	1720 (C=O), 1650 (C=N), 1580 (C=C)	208 (4,23), 250 (4,21)
IVe	4,26, s (2H); 4,68, s (2H); 8,01—8,32, q (4H)	1690 (C=O), 1640 (C=N), 1580 (C=C)	206 (4,0), 216 (3,86) i*, 280 (4,02)
IVf	3,92, s (3H); 3,93, s (3H); 4,20, s (2H); 4,61, s (2H); 6,86—7,60, m (3H)	1710 (C=O), 1650 (C=N), 1580 (C=C)	211 (4,35), 217 (4,33) i 261 (4,11), 293 (3,79)
IVg	1,48, d 7,5 (3H); 4,09, m (1H); 4,54, d 18 (1H); 4,65, q 18,2 (1H); 7,3—7,97, m (5H)	1710 (C=O), 1630 (C=N), 1580 (C=C)	208 (4,23), 238 (4,22)
IVh	1,02, t 7,5 (3H); 1,91, m (2H); 3,98, m (1H); 4,51, d, 18 (1H); 4,62, q 18,2 (1H); 7,3—7,97, m (5H)	1710 (C=O), 1630 (C=N), 1570 (C=C)	208 (4,24), 239 (4,20)
IVi	3,15, q 14,6, 6 (1H); 3,27, q 14,4, 8 (1H); 4,12, d 18 (1H); 4,33 m (1H); 4,52, q 18, 1,95 (1H); 7,05—7,99, m (10H)	1710 (C=O), 1640 (C=N), 1580 (C=C)	208 (4,38), 240 (4,12)
IVj	3,19, q 14,7 (1H); 3,29, q 14,5, 6 (1H); 3,93, d (6H); 4,16, d 18 (1H); 4,36, m (1H); 4,51, q 18, 1,95 (1H); 6,75—7,60, m (8H)	1720 (C=O), 1640 (C=N), 1580 (C=C)	210 (4,32), 217 (4,29) i 265 (3,96), 295 (3,75)

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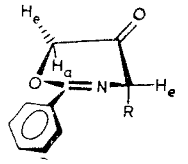
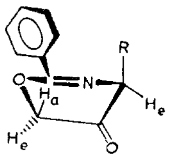
*Note: i indicates an inflection.

Oxazines IVa-j are formed in high yields and are obtained as yellowish crystalline substances when R^1 = H. The introduction of a substituent in the 4 position of the oxazine ring leads to a decrease in the melting point (IVg-j are oily substances; see Table 2).

The structures of oxazines IV are confirmed unambiguously by their spectral characteristics (Table 1). The molecular-ion peaks correspond to the calculated values. Absorption bands characteristic for the C=O group in ketones, as well as bands of C=N and C=C bonds, are observed in the IR spectra. The signals of the protons of the 6-(H_a + H_e) methylene group are observed in the PMR spectra of IVa-f in the form of singlets and are shifted to weaker field as compared with the singlet of the 4-(H_a + H_e) protons. When a substituent is introduced in the 4 position (IVg-j), the protons attached to C_6 become nonequivalent, and the signal is converted to two doublets with geminal coupling constant $J_{a,e}$ = 18 Hz; weak splitting of one of them due to spin—spin coupling with the 4-H methylidyne proton (J = 1.95 Hz) is observed in this case. When the signal of the methylidyne proton is suppressed, this splitting vanishes. The constant with a value of ~2 Hz is characteristic for coupling of protons with an equatorial—equatorial orientation that are separated by a carbonyl group, and the axial—equatorial and axial—axial coupling constants are considerably smaller [2]. This constitutes evidence that the substituent attached to C_4 is axially oriented; this in turn is evidently a consequence of the stereoselectivity of the intramolecular cyclization of diazo ketones I. It is known that a distorted boat conformation is characteristic for 1,3-oxazines [3]. Taking this into account, the following structures can be proposed for oxazines IVg-j:





Thus, the intramolecular cyclization of benzoylated aminoalkyl-α-diazo ketones discovered in this research is a new and convenient method for the synthesis of difficult-to-obtain 1,3-oxazine derivatives.

TABLE 2. Oxazines IV

Compound	mp, °C	N found, %	Empirical formula	N calculated, %	Yield, %
IVa	92—93	8,1	$C_{10}H_9NO_2$	8,0	90
IVb	104	7,5	$C_{11}H_{11}NO_2$	7,4	76
IVc	75—76	6,8	$C_{10}H_8ClNO_2$	6,7	75
IVd	93—95	5,5	$C_{10}H_8BrNO_2$	5,5	73
IVe	130—132	12,8	$C_{10}H_8N_2O_4$	12,7	64
IVf	142	5,9	$C_{12}H_{13}NO_4$	6,0	73
IVg	88—90*	7,5	$C_{11}H_{11}NO_2$	7,4	85
IVh	62—63*	7,0	$C_{12}H_{13}NO_2$	6,9	79
IVi	102—103*	5,4	$C_{17}H_{15}NO_2$	5,3	78
IVj	138—139	4,4	$C_{19}H_{19}NO_4$	4,3	76

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*Picrate.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord IR-75 spectrometer. The UV spectra of solutions in methanol were recorded with a Specord UV-Vis spectrophotometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Bruker WH-360 spectrometer with tetramethylsilane as the internal standard. The purity of the substances was monitored by thin-layer chromatography (TLC) in an ethyl acetate—benzene system on Silufol UV-254 plates.

2-Aryl-5,6-dihydro-4H-1,3-oxazin-5-ones (IVa-d, f-j, General Method). A 3-mmole sample of diazo ketone I was dissolved in 30 ml of chloroform, 600 mg (6 mmole) of concentrated H_2SO_4 was added, and the mixture was shaken vigorously, during which vigorous nitrogen evolution and rapid decolorization of the solution were observed. The mixture was then neutralized with sodium bicarbonate, 10 ml of water was added, and the chloroform layer was separated and dried over Na_2SO_4. The solvent was removed, and the residue was washed with cold ether and dried.

2-(4-Nitrophenyl)-5,6-dihydro-4H-1,3-oxazine-5-one (IVe). This compound was similarly obtained; however, the chloroform layer was separated after neutralization, and the product was isolated by filtration of the aqueous layer. The residue was washed with water and dried.

The compounds obtained were chromatographically individual and did not require further purification. Their properties are presented in Table 2.

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