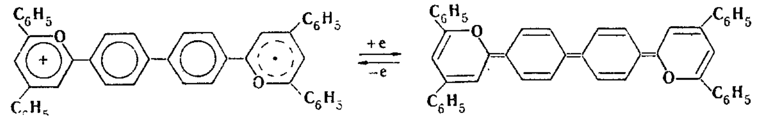
1,3,4-Trisubstituted 2-benzopyrylium cations (XI, XIII) are reduced completely reversibly; the coefficient of reversibility drops sharply if the 4 position is unoccupied (X, XIII), and this indicates dimerization of the corresponding free radicals.

The reduction of dipyrylium salts proceeds in a peculiar manner (Table 3). In all cases in which both pyrylium rings are directly connected or are connected through a conducting chain (XVIII) the reduction process in two waves with a high degree of reversibility. It follows from this that the first step in the reduction is the formation of stable cation radicals of the previously studied [1] type of the cation radical from bis-2,6-di-tert-butylpyrylium. Subsequent reduction leads to a dipyranylidene structure, for example:



Dications with a broken conjugation chain (XX-XXII) are reduced in one two-electron wave; consequently, in this case one will hardly be able to isolate any cation radicals.

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SYNTHESIS AND SOME TRANSFORMATIONS OF 4-OXO-2-(β-ETHOXYVINYL)-4H-1,3-BENZOXAZINIUM SALTS

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UDC 547.867.2.07

A method was developed for the synthesis of 4-oxo-(β-ethoxyvinyl)-4H-1,3-benzoxazinium salts by condensation of oxo-2-alkylbenzoxazinium salts by condensation of oxo-2-alkylbenzoxazinium salts with ethyl orthoformate. During hydrolysis and aminolysis, attack of the nucleophile is directed to the β-carbon atom of the benzoxazinium salts. The previously unknown 2-formylmethylene-4-oxo-3,4-dihydro-2H-1,3-benzoxazines and their nitrogen derivatives were obtained.

In the present research it was shown the 2-alkyl-4-oxo-4H-1,3-benzoxazinium salts [1] react exceptionally readily with ethyl orthoformate to give 2-(β-ethoxyvinyl)-substituted oxobenzoxazinium salts (II, Table 1). The reaction is accomplished by brief heating of perchlorates Ia-d and ethyl orthoformate (1:2) in a mixture of acetic anhydride and nitro-

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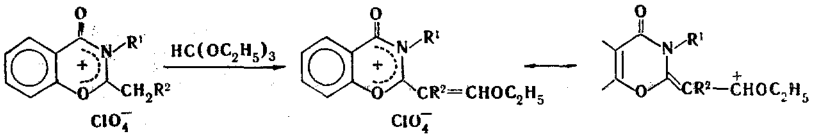
methane (1:2.5) at 50°C. Orthoacetic and orthooxalate esters do not react under these conditions.



I a-d A II a-d B

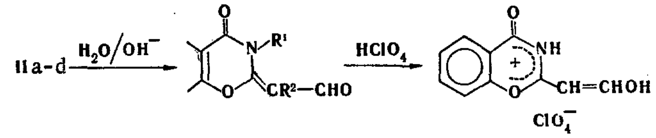
I, II a-c R^2=H; a R^1=H; b R^1=CH_3; c R^1=C_6H_5; I, II d R^1=H, R^2=CH_3

The structures and individuality of salts II were confirmed by IR and PMR spectroscopy. Thus the PMR spectrum of perchlorate IIa contains, in addition to the typical signal of the ethyl group, two doublets (5.82 and 8.42 ppm) with a vinyl proton spin–spin coupling constant (SSCC) of 11.5 Hz.

In the IR spectra of perchlorates II, in addition to the bands characteristic for this class of compounds [1], a band at 1610 cm^{-1} (C=C) and an intense band at 1190-1265 cm^{-1}, assignable to the stretching vibrations of an ether group, sometimes appear. As compared with oxo-2-alkylbenzoxazinium salts, the characteristic band of carbonyl absorption of the oxooxazinum cation is shifted by 30 cm^{-1} to the low frequency region and appears at 1740 cm^{-1}.

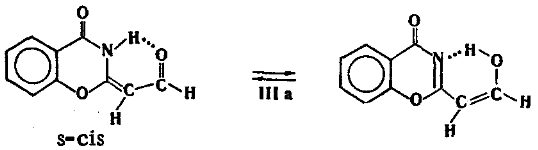
The reactive of ethoxyvinyl salts II with respect to some nucleophilic reagents were studied. It has previously been shown that 2-alkyl-, 2-aryl- [1], and 2-styryl-substituted [2] oxobenzoxazinium salts react readily with opening of the heteroring. However, in contrast to these compounds, in 2-β-ethoxyvinyl derivatives the reaction center is transferred from the ring 2-C atom to the β-carbon atom of the double bond because of the considerable contribution of mesomeric form B. This assumption is confirmed by the resonance of the β-vinyl proton (in the PMR spectra) at weaker field (8.42 ppm) as compared with the α-vinyl protons; this attests to partial localization of the positive charge on the β-carbon atom and explains the difference in the directions of the reactions.

α,β-Unsaturated aldehydes of the oxazinone series (III) are formed when perchlorates IIa-d are treated with water or a weakly alkaline solution (see Table 2).



IIIa-d IV

In this case, if R^1 = H, two tautomeric forms — the aldehyde and the enol forms — are possible:



A comparison of the IR spectra of IIIa and IIIb, c (the fixed aldehyde forms) showed their similarity, and this indicates that IIIa (in the condensed phase) exists in the aldehyde form (in the condensed phase). Strong absorption bands of aldehyde (∼1705 cm^{-1}) and amide (∼1665 cm^{-1}) groups and the absorption bands of a double bond (1610-1625 cm^{-1}) are present in the IR spectra of IIIa-c. Compound IIId evidently exists in the enol form, as indicated by the position of the frequency of the carbonyl absorption ($\nu_{C=O}$ 1685 cm^{-1}) characteristic for benzoxazinones [3].

The presence in the PMR spectrum of IIIa of two distinct doublets (J = 3 Hz), together with the position of the resonance signal of the β-proton (9.07 ppm), constitutes evidence that this compound in solution also exists in the aldehyde s-cis form, stabilized by an intramolecular hydrogen bond. Aldehyde IIIb, intramolecular stabilization in which is impossible,

TABLE 1. 2[β-Ethoxy(hydroxy)vinyl]- and 2-(β-Aminovinyl)-4-oxo-4H-1,3-benzoxazinium Perchlorates (II, IV, V, VI, and X)

Compound	Color	mp, °C*	Found, %				Empirical formula	Calc., %				IR spectra† (characteristic frequencies, cm⁻¹)									Yield, %
			C	H	Cl	N		C	H	Cl											
IIa	Yellow-orange	145—148	44,8	4,1	12,0	4,6	$C_{12}H_{12}ClNO_7$	45,4	3,8	11,2	4,4	3170		1752 (ш.)	1739	1630	1610	1579	1500	1220	63
IIb	Yellow-green	142—144	46,0	4,5	10,9	4,4	$C_{13}H_{14}ClNO_7$	47,1	4,2	10,7	4,2				1745	1630		1590	1533	1265	48
IIc	Yellow	170—172	53,5	4,2	8,5	3.8	$C_{18}H_{16}ClNO_7$	54,9	4,1	9,0	3,6				1740	1635	1610		1512	1225	55
IId	Light-yellow	155—157	46,1	4,6	10,8	4.2	$C_{13}H_{14}ClNO_7$	47,1	4,2	10,7	4,2		3280		1742	1625		1554	1500	1190	8,3
IV	Yellow	120—122	41.9	3,2	11,4	5.2	$C_{10}H_8ClNO_7$	41,4	2.8	12,2	4,8		3500		1724	1630		1570	1492		67
Va	Yellow	255—257	52,3	3,6	9.2	7.8	$C_{16}H_{13}ClN_2O_6$	52,7	3,6	9,7	7,7	3300	3220	3150	1721		1630	1596	1563		100
Vb	Yellow	237—239	51.5	4,3	9,0	7.1	$C_{17}H_{15}ClN_2O_7$	51,8	3,6	9,0	7.1	3300	3210	3140	1721	1648	1630	1600	1580		73
Vc	Yellow	219—220	51,4	3,9	8,9	7,0						3305	3205	3140	1720	1660	1633	1597			60
Vd	Orange	239—240	52,2	4,1	8,7	7,1						3315	3230	3150	1714	1647	1630	1607	1578		85
Ve	Yellow	230—231	54.1	4,5	9,8	7,4	$C_{17}H_{15}ClN_2O_6$	54,0	4,0	9,4	7,4		3200		1720		1625	1589	1565		75
Vf	Yellow	235—236	54,5	4.0	8,9	7,1							3140		1725	1660	1634		1565		47
Vg	Yellow	244—245	54.5	4.1	9,4	6,9							3140		1720	1658	1624		1568		52
Vh	Lemon-yellow	245—246	49,7	3,6	8,9	6,5	$C_{17}H_{13}ClN_2O_8$	50,0	3.2	8,6	6.8		3100	1738	1716	1660	1630	1612	1575		100
Vi	Yellow	256—257	54,5	4.2	9,1	7,5	$C_{17}H_{15}ClN_2O_6$	54,0	4,0	9.4	7.4				1735	1645	1625	1596	1560		67
Vj	Yellow	239—241	60,1	4,4	8,2	6,7	$C_{22}H_{17}ClN_2O_7$	60.0	3,9	8.1	6.4				1740	1650	1630	1595	1535		33
VI	Yellow	177—178	50,2	3,8	9,3	10,2	$C_{16}H_{14}ClN_3O_6$	50.6	3,7	9,4	10,5		3400		1700		1618	1590	1540		69
X	Yellow	170—171	50,7	5,0	10,0	7,5	$C_{15}H_{17}ClN_2O_6$	50,6	4,5	9,9	7,8		3100		1726		1636	1605	1502		54

*Compounds IV, Vb-g,j, VI, and X were crystallized from glacial acetic acid, Va,i were crystallized from glacial acetic acid and nitromethane, and Vh was crystallized from dimethylformamide.

†A low-intensity broad absorption band of the ClO_4^- ion is present in the spectra of all of the perchlorates at 1010-1123 cm⁻¹.

TABLE 2. 2-Formylmethylene-4-oxo-3,4-dihydro-2H-1,3-benzoxazines (III) and Their Nitrogen Derivaties (VII, VIII, and IX)

Compound	Color	mp, °C*	Found, %			Empirical formula	Calc., %			IR spectra (characteristic frequencies, cm^{-1})	Yield, %
			C	H	N		C	H	N		
IIIa	Light-yellow	143—144	63,2	3,8	7,4	$C_{10}H_7NO_3$	63,5	3,7	7,4	1710 1660 1610 1556	62
IIIb	Colorless	166—167	64,4	4,3	6,9	$C_{11}H_9NO_3$	64,7	4,9	6,9	1705 1665 1625 1600 1540	100
IIIc	Colorless	165	72,2	4,3	5,6	$C_{16}H_{11}NO_3$	72,5	4,2	5,3	1700 1665 1625 1590 1510	35
IIId	Light-green	163—164	64,7	4,6	6,9	$C_{11}H_9NO_3$	64,7	4,9	6,9	3150 1685 1630 1600(sh) 1560	77
VIIa	Yellow	235—240	72,7	4,4	10,2	$C_{16}H_{12}N_2O_2$	72,7	4,5	10,6	1658 1614 1589 1542 1496 1278	81
VIIb	Light-yellow	142—144	69,1	5,1	9,3	$C_{17}H_{14}N_2O_3$	68,7	5,1	9,5	1660 1625(sh) 1580 1510 1300	98
VIIc	Lemon	184—185	68,8	5,5	9,4					1740 1696 1655 1610 1595 1307	57
VIId	Yellow	163—164	68,8	4,8	9,6					1672 1640 1622 1600 1541 1300	67
VIIe	Lemon	191—192	73,1	4,8	10,0	$C_{17}H_{14}N_2O_2$	73,4	5,0	10,0	1689 1640 1590 1510 1300	100
VIII	Flesh-colored	155—157	68,9	5,2	14,8	$C_{16}H_{13}N_3O_2$	69,3	4,7	15,1	3250 1685 1610 1560 1545 1500 1300	60
IX	Yellow	172—173	63,3	4,1	14,9	$C_{10}H_8N_2O_2$	63,8	4,3	14,9	3300 3100 1670 1640 1621 1590 1547 1524 1512 1260	62

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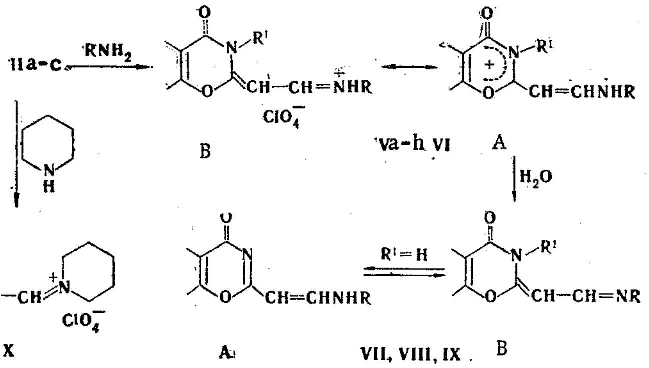
*Compounds IIIa,b were crystallized from methanol, IIIc,d, VIIb-e, and IX were crystallized from ethanol, V was crystallized from dimethylformamide, and VIII was crystallized from benzene.

probably exists in the transoid conformation (J = 8 Hz).

Aledhyde IIIa is protonated on treatment with anhydrous perchloric acid and is converted to oxo-2-(β-hydroxyvinyl)benzoxazinium salt IV (see Table 1).

In the reaction of perchlorates IIa-c with aromatic amines and piperidine the ethoxy group is replaced by an amino group to give the corresponding aminovinyl salts V and X.



V, VIIa-h $R^1=H$; a $R=C_6H_5$; b-d and e-g, respectively, R=2-, 3-, 4-$CH_3OC_6H_4$ and 2-, 3-, 4-$CH_3C_6H_4$; h $R=4\text{-}HOOCC_6H_4$; V, VII i,j $R=C_6H_5$; i $R^1=CH_3$; j $R^1=C_6H_5$; VI, VIII $R^1=H$, $R=NHC_6H_5$; IX $R^1=R=H$

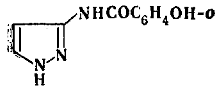
2-β-Arylaminovinyl salts V can be obtained directly by reaction of equimolar amounts of oxo-2-alkylbenzoxazinium perchlorate, ethyl orthoformate, and an aromatic amine (the yield of Va from salt IIa was quantitative).

In addition to the bands at 1720 and 1630 cm^{-1} characteristic for oxobenzoxazinium salts [1], an intense band at 1560 cm^{-1} (probably the absorption of a polarized C=N bond) appears in the IR spectra of the β-arylaminovinyl derivatives (see Table 1). The decrease in the frequency of the carbonyl absorption as compared with oxo-2-alkyl(aryl)benzoxazinium salts is explained by the considerable contribution of mesomeric form B, the preferableness of the realization of which was previously demonstrated in the case of model compounds — oxo-2-(β-dimethylaminovinyl)benzoxazinium perchlorates.

When perchlorates V are treated with inorganic bases, perchloric acid is split out (usually with difficulty), and the corresponding bases VII are formed (see Table 2). Compound IX was obtained by treatment of β-ethoxyvinyl compound IIa with concentrated ammonium hydroxide.

A comparison of the IR spectra of bases VII and IX and of the corresponding aldehydes IIa-c evidently indicates that they exist in the condensed phase in imine form B. The absorption of the NH bond cannot be observed in the spectra of aldehydes IIIa-c and their nitrogen derivatives VII in the shortwave region because of the formation of a strong intramolecular hydrogen bond. Low-intensity broad absorption bands with maxima at 3300 and 3100 cm^{-1} appears in the spectrum of IX.

In the case of the reaction of β-ethoxyvinyl salt IIa with hydrazine and phenylhydrazine we attempted to ascertain the prospects for the use of difunctional amines. It was shown that the reaction with phenylhydrazine proceeds via the usual scheme to give perchlorate VI, whereas pyrazole XI, the structure of which was confirmed by IR and PMR spectroscopy, is formed with hydrazine.



XI

EXPERIMENTAL

The PMR spectra were recorded with a Tesla-Bs-487-C spectrometer (80 MHz) with hexamethyldisiloxane as the standard. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

4-Oxo-2-(β-ethoxyvinyl)-4H-1,3-benzoxazinium Perchlorate (IIa). A mixture of 2.61 g (10 mmole of perchlorate Ia, 3-6 ml of ethyl orthoformate, 4 ml of acetic anhydride, and 10 ml of nitromethane* was heated until all of the solid dissolved (50-60°), after which it was cooled rapidly and diluted with a threefold excess of ether. The precipitated perchlorate was removed by filtration and washed once with the minimum amount of glacial acetic acid and three to four times with ether to give 2.2 g (66%) of a product with mp 145-148°.

Perchlorates IIb,c (see Table 1) were similarly obtained from the corresponding salts I. In the preparation of perchlorate IId, the reaction mixture was heated on a water bath (50°) for 3 min, after which it was cooled rapidly and treated with 1-1.5 ml of ether. The precipitated salt was removed by filtration. PMR spectrum (in CF_3COOH) of perchlorate IIa: 1.10 (t, CH_2CH_3), 4.18 (q, CH_2CH_3) 5.82 and 8.42 (d, J = 11.5 Hz), and 7.22-7.90 ppm (m, phenylene). PMR spectrum of perchlorate IIb: 1.10 (t), 4.22 (q), 2.75 (s, $N-CH_3$), 5.75 and 8.45 (d, J = 11.5 Hz), and 7.12-8.00 ppm (m), PMR spectrum of perchlorate IId: 1.08 (t), 1.70 (s, $\alpha-CH_3$), 4.27 (q), 7.12-7.92 (m), and 8.42 ppm (s, β-CH).

2-Formylmethylene-4-oxo-3,4-dihydro-2H-1,3-benzoxazine (IIIa). A 1-2 ml sample of sodium acetate solution or 3 ml of water was added to a solution of 1.59 g (5 mmole) of perchlorate IIa in 3 ml of acetone, after which the product was removed by filtration and washed with the minimum amount of methanol and three to four times with ether to give 0.6 g (62%) of light-yellow needles with mp 143-144°. PMR spectrum (in nitromethane):

Compounds IIIb-d were similarly obtained (see Table 2). PMR spectrum of aldehyde IIIb (in DMSO): 2.52 and 7.50 (d, J = 8 Hz) and 4.72-5.55 ppm (m, phenylene). In contrast to aldehydes IIIa-c, IIId gave a dark-brown coloration with an alcohol solution of ferric chloride.

2-(β-Hydroxyvinyl)-4-oxo-4H-1,3-benzoxazinium Perchlorate (VI). A solution of 0.1 ml (1 mmole) of 70% $HClO_4$ in 0.4 ml of acetic anhydride was added to a suspension of 0.19 g (1 mmole) of aldehyde in 3 ml of glacial acetic acid, after which the product was removed by filtration and washed with ether to give 0.2 g (67%) of a product with mp 120-122°.

2-(β-Anilinovinyl)-4-oxo-4H-1,3-benzoxazinium Perchlorate (Va). A) A 0.93-g (10 mmole) sample of aniline was added to a solution (prepared by heating) of 3.17 g (10 mmole) of perchlorate IIa in 10 ml of nitromethane or glacial acetic acid, and the mixture was heated to the boiling point.† The crystals that separated out when the mixture was cooled‡ were removed by filtration and washed with the minimum amount of glacial acetic acid and three to four times with ether. An additional amount of substance could be isolated by dilution of the filtrate with ether. The overall yield of product with mp 255-257° was 3.42 g (94%).

Perchlorates Ve-h were similarly obtained (see Table 1).

B) A 2.61-g (10 mmole) sample of perchlorate Ia was dissolved in 6 ml ethyl formate and 10 ml of nitromethane, and 0.93 g (10 mmole) of aniline was added. The mixture was heated to the boiling point, after which it was cooled rapidly and diluted with ether. Workup gave 3.64 g (100%) of a product with mp 255-257°.

2-(β-Piperidinovinyl)-4-oxo-4H-1,3-benzoxazinium Perchlorate (X). A 0.1-ml (1 mmole) sample of piperidine was added to a hot solution of 0.3 g,(1 mmole) of perchlorate IIa in 2 ml of tetrachlorethane, after which the mixture was cooled rapidly and diluted with ether. The liberated oil began to crystallize on standing. Workup gave 0.18 g (53%) of yellow crystals with mp 170-171°.

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*Replacement of nitromethane by glacial acetic acid or tetrachlorethane, in which a higher temperature is required for complete dissolving of the starting salt, leads to contamination of perchlorates II because of their subsequent transformations. Attempts to crystallize the synthesized salts from most polar solvents also lead to their contamination.

†In the preparation of perchlorates Vb-d,i,j (see Table 1), the reaction mixture was cooled after the addition of the amine.

‡In some cases an oil was liberated; the oil began to crystallize on standing (10-15 min).

2-(β-Anilinovinyl)-4-oxo-3,4-dihydro-2H-1,3-benzoxazine (VIIa). A 3.64-g (10 mmole) sample of perchlorate Va was dissolved in the minimum amount of acetone, and 2.5 ml of water or a 10% sodium carbonate solution was added slowly. The reaction product was removed by filtration, washed with nitromethane, and recrystallized from dimethylformamide (DMF) to give 2.14 g (81%) of a product with mp 235-240°.

Compounds VIIb,e (see Table 2) were obtained by treatment of the corresponding salts V with excess sodium carbonate solution. In the preparation of VIIc, the corresponding perchlorate was refluxed in excess 10% sodium carbonate solution for 1 h (in the preparation of VIId, the reaction mixture was heated on a boiling-water bath).

Perchlorates V are extremely stable and sometimes (particularly when $R^1 \neq H$) do not undergo any change even when they are dissolved in a strongly alkaline solution.

2-(β-Aminovinyl)-4-oxo-4H-1,3-benzoxazine (IX). This compound was obtained in 62% yield as yellow crystals with mp 172-173° by treatment of perchlorate IIa with concentrated ammonium hydroxide.

2-Formylmethylene-4-oxo-2H-1,3-benzoxazine Phenylhydrazone Perchlorate (VI). A 0.17-g (16 mmole) sample of phenylhydrazine was added to a suspension of 0.51 g (16 mmole) of perchlorate IIa in 2 ml of nitromethane, and the mixture was cooled and diluted with a twofold amount of ether. Workup gave 0.42 g (69%) of yellow crystals with mp 177-178°.

2-Formylmethylene-4-oxo-2H-1,3-benzoxazine phenylhydrazone (VIII) was obtained in 60% yield as flesh-colored crystals with mp 155-157° by treatment of perchlorate VI with 10% $NaHCO_3$ solution.

Compounds VII-IX did not give a coloration with an alcohol solution of ferric chloride.

3-Salicyloylaminopyrazole (XI). A 0.2-ml (2 mmole) sample of hydrazine hydrate was added dropwise to a solution of 0.3 g (1 mmole) of perchlorate IIa in 2 ml of glacial acetic acid, and the resulting solution was heated to the boiling point. It was then cooled and treated with 2 ml of water, and the resulting precipitate was removed by filtration to give 0.6 g (62%) of anhydrous crystals with mp 242-243°. IR spectrum: 3265, 1650 (amide C=O), 1609, 1580, 1495 cm^{-1}. PMR spectrum (in CF_3COOH): 6.18 and 7.62 (doublets, J = 3.4 Hz, CH=CH), 6.58-7.55 ppm (m, phenylene). The product gave a violet coloration with an alcohol solution of ferric chloride. Found: C 59.6; H 4.7; N 19.2%. $C_{10}H_9N_3O_2$. Calculated C 59.1; H 4.4; N 20.6%.

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