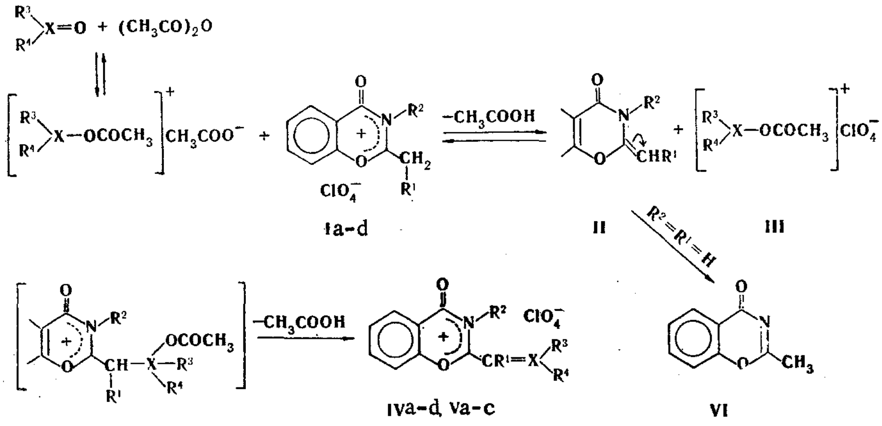
CONDENSATION OF 2-ALKYL-4-OXO-1,3-BENZOXAZINIUM SALTS WITH CARBONYL COMPOUNDS AND THEIR HETEROANALOGS

V. V. Mezheritskii, L. G. Minyaeva,
Yu. I. Ryabukhin, and G. N. Dorofeenko

UDC 547.867.2.07:542.953

A method is proposed for the synthesis of 2-(β-dimethylaminovinyl)-4-oxo-1,3-benzoxazinium salts and dimethyl(4-oxo-3H-1,3-benzoxazine-2-methylene)sulfonium salts by condensation of 2-alkylbenzoxazinonium salts with dimethylformamide and dimethyl sulfoxide.

Considering the exceptional ease of the reaction of 2-alkylbenzoxazinonium salts with aromatic aldehydes and ethyl orthoformate [1], we attempted to ascertain the possibility of condensation of these salts with other carbonyl compounds and their heteroanalogs.



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

In the present research it was shown that 2-alkyl-substituted benzoxazinonium salts Ia-d [2] readily react with dimethylformamide (DMF, by refluxing) and dimethyl sulfoxide (DMSO, at room temperature) to give the previously undescribed 2-(β-dimethylaminovinyl)-4-oxo-1,3-benzoxazinium (IV) and dimethyl(4-oxo-3H-1,3-benzoxazine-2-methylene)sulfonium (V) salts, respectively, in high yields. The condensation was carried out in acetic anhydride, which, in analogy with similar reactions in the case of pyrylium salts, should lead to activation of the components. Data on the yields and properties of the compounds obtained are presented in Table 1.

In addition to the absorption bands characteristic for benzoxazinonium salts [2], a band at 1647 cm^{-1} (C=C) and an intense band at 1558-1590 cm^{-1} (evidently the absorption of a polarized C=N bond) appear in the IR spectra of 2-β-dimethylaminovinyl derivatives IV. The shift of the frequency of the carbonyl absorption to lower frequencies by 20-45 cm^{-1} in the spectra of immonium salts IV and sulfonium salts V as compared with the starting compounds is due to additional stabilization of the oxazinonium cation because of delocalization:

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 328-331, March, 1977. Original article submitted Feburary 12, 1976.

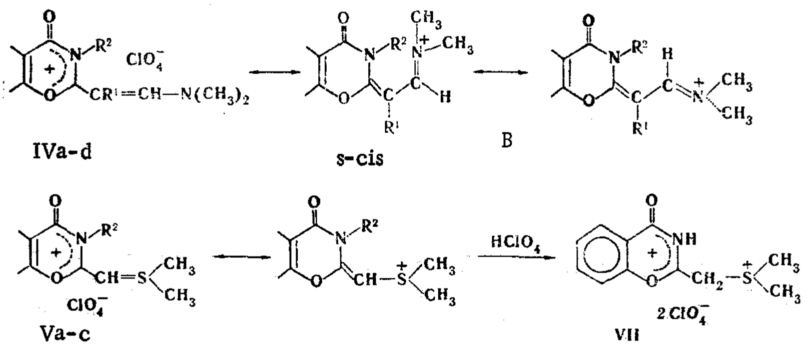
TABLE 1. 2-(β-Dimethylaminovinyl)-4-oxo-1,3-benzoxazinium (IV) and Dimethyl(4-oxo-3H-1,3-benzoxazine-2-methylene)sulfoniu (V) Perchlorates

Compound	$X\langle^{R^3}_{R^4}$	R^1	R^2	mp, °C*	Empirical formula	Found, %					Calc., %					IR spectra, † ν, cm^{-1}	Yield, %
						C	H	Cl	N	S	C	H	Cl	N	S		
IVa	$CHN(CH_3)_2$	H	H	197	$C_{12}H_{13}ClN_2O_6$	45,0	4,5	10,7	8,4		45,5	4,1	11,2	8,8		3480, 1729, 1640, 1607, 1600, 1590, 1518	38
IVb	$CHN(CH_3)_2$		CH_3	290	$C_{13}H_{15}ClN_2O_6$	47,6	4,4	10,9	8,5		47,2	4,5	10,7	8,5		1727, 1647, 1626, 1600, 1572	85
IVc	„ „		C_6H_5	212—213	$C_{19}H_{20}ClN_2O_6$	55,0	4,5	9,2	7,1		55,0	4,3	9,0	7,2		1748, 1735 (sh), 1647, 1629, 1598, 1560	92
IVd	„ „	CH_3	H	209—210	$C_{13}H_{15}ClN_2O_6$	47,5	4,6	10,5	8,3		47,2	4,5	10,7	8,5		3170, 1708, 1652, 1622, 1597, 1574, sh), 1558	81
Va	$S(CH_3)_2$		H	151—152	$C_{11}H_{12}ClNO_6S$	40,9	3,7	11,0	4,4	9,9	40,3	3,7	11,0	4,2	9,6	1708, 1660, 1630, 1610, 1575, 1521	93
Vb	$S(CH_3)_2$		CH_3	191—192	$C_{12}H_{14}ClNO_6S$	42,9	4,2	10,8	4,2	9,5	42,5	4,4	10,6	4,4	8,5	1760 sh), 1748, 1632, 1590, 1537	53
Vc	„ „		C_6H_5	188	$C_{17}H_{16}ClNO_6S$	51,4	4,3	8,9	3,6	7,8	51,3	4,0	8,9	3,5	8,0	1712, 1635, 1602, 1589, 1500	80

---

*Compounds IVa-d were crystallized from glacial acetic acid.

†An intense band of stretching vibrations of the perchlorate ion is present in the IR spectra of all of the compounds at 1100 cm^{-1}.



IVa-d s-cis B

Va-c VII

An investigation of the PMR spectra of IV (see Table 2) showed that of the two possible mesomeric forms A and B, the B form is realized, and the compounds evidently exist in the most stable cisoid conformation: the spectra display the presence of two nonequivalent methyl groups, the chemical shifts of which differ by ~0.25 nm because of the absence of free rotation about the carbon–carbon single bond. The existence of the compounds in mesomeric form A because of the absence of double bond character of the C–N bond would be expressed in terms of equivalence of the methyl groups.

In contrast to the transoid conformation, in the s-cis conformation the protons of the methyl group in the cis orientation relative to the ring give a signal at stronger field because of the magnetic anisotropy of the heteroring. When a phenyl ring, which induces an additional magnetic field, is introduced in the 3 position of the heteroring, a shift in the signal of the s-cis-methyl group to stronger field by 25 Hz is observed, whereas this effect is not exerted on the position of the signal of the s-trans-methyl group because of its remoteness. The PMR spectra of IV also contain two doublets of vinyl protons, and the doublet in the low-field portion of the spectrum corresponds to the β-vinyl porton, as seen from its broadening and partial splitting because of the long-range coupling with the protons of the methyl groups. The high-field doublet belongs to the α-proton; this is confirmed by its shift to stronger field when a phenyl substitutent (IVc), which increases the conjugation, is introduced.

Because of mesomeric stabilization, IV and V are considerably more stable than 2-alkyl-, aryl-, and styrylbenzoxazinonium salts, as attested to by their behavior under hydrolysis conditions. Thus perchlorates IV and V do not undergo any changes when they are dissolved in water or a weakly alkaline ($NaHCO_3$) solution. However, the heteroring undergoes cleavage to salicylamide when these salts are refluxed for a long time (4 h) in water or 5% NaOH solution.

Sulfonium salts V have sufficient basicity and are protonated on treatment with perchloric acid to give diperchlorates VII.

2-Alkylbenzoxazinonium salts do not react with ketones, p-quinone, isomethyl nitrite, and carboxylic acid chloride and esters; the reaction with p-nitrosodimethylaniline, N,N-dimethylacetamide, and pyridine N-oxide stops at the step involving the formation of intermediate cations III, the electrophilicities of which are probably inadequate for subsequent condensation. The benzoxazinone (VI) isolated in this case is evidently formed as a result of migration of a proton from methylene base II.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with a Tesla BS 487C 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.

2-(β-Dimethylaminovinyl)-4-oxo-1,3-benzoxazinium Perchlorate (IVa). A 1.0-g (0.013 mole) sample of DMF was added to a suspension of 1.31 g (0.005 mole) of perchlorate Ia in 5 ml of acetic anhydride, and the mixture was heated to the boiling point. It was then cooled, and the precipitated product was removed by filtration and washed with ether to give 0.6 g (38%) of a product with mp 197° (dec., from glacial acetic acid).

TABLE 2. PMR Spectra of 2-(β-Dimethylaaminovinyl)-4-oxo-1,3-bnezoxazinium Perchlorates* in Trifluoroacetic Acid (20°C), ppm

Compound	s-cis-CH_3, (s)†	s-trans-CH_3, (s)	N—CH_3, (s)	H_{α}, (d)	H_{β}, (d)	$J_{CH=CH}$, (Hz)	Aromatic protons (m)
IVa	2,93	3.18		5.07	8,07	11,5	7,0—7,8
IVa‡	3,01	3.32		5.15	—	11,5	—
IVb	3.00	3.25	3,21	5,05	8,20	11,5	6,92—7,75
IVc	2,60	3,12		4,32	8.15	11.5	6,95—7,87

*The spectra of sulfonium salts V could not be recorded because of their low solubilities.

†Here and subsequently, s is singlet, d is doublet, and m is multiplet.

‡In HCOOH.

Perchlorates IVb,d (see Table 1) were obtained as light-yellow crystals.

2-(β-Dimethylaminovinyl)-3-phenyl-4-oxo-1,3-benzoxazinium Perchlorate (IVc). This compound was obtained by refluxing (for 15-20 min) a mixture of 1.7 g (0.005 mole) of perchlorate Ic, 5 ml of acetic anhydride, and 1.0 g (0.013 mole) of DMF. The reaction mixture was cooled, diluted with ether, and allowed to stand overnight in a refrigerator. The initially liberated oil began to crystallize. Workup gave 1.8 g (92%) of a product with mp 212-213° (dec., from glacial acetic acid).

Dimethyl(4-oxo-3H-1,3-benzoxazine-2-methylene)sulfonium Perchlorate (Va). A 0.78-g (0.01 mole) sample of DMSO was added to a suspension of 2.61 g (0.01 mole) of perchlorate Ia in 5 ml of acetic anhydride, during which the mixture became warm. It was then cooled and worked up to give 3.0 g (93%) of colorless crystals of Va with mp 151-152° (dec.).

Perchlorates Vb,c (colorless crystals) were similarly obtained (see Table 1) in a mixture of acetic anhydride and nitromethane (1.25:1).

Dimethyl(4-Oxo-1,3-benzoxazinium-2-methyl)sulfonium Diperchlorate (VII). A solution of 0.25 ml (0.0025 mole) of 70% perchloric acid in 0.8 ml of acetic anhydride was added to a suspension of 0.8 g (0.025 mole) of perchlorate Va in 3 ml of nitromethane and 1 ml of glacial acetic acid. The product, which formed in 2-3 min, was removed by filtration to give 0.9 g (86%) of colorless crystals, which decomposed explosively at 210°.

2-Methyl-4H-1,3-benzoxazin-4-one (VI). A twofold amount of DMF or N,N-dimethylacetamide was added to a suspension of perchlorate Ia in acetic anhydride, and the mixture was allowed to stand overnight. The precipitated product was removed by filtration and recrystallized from benzene to give VII, with mp 217° (mp 217° [3]), in 50% yield.

Reaction of Perchlorate Ia with p-Nitrosodimethylaniline and Pyridine N-oxide. An equimolar amount of p-nitrosodimethylaniline was added to a suspension of the perchlorate in acetic anhydride, and the product, which formed in 5-10 min, was removed by filtration and washed with ether to give 0.9 g (62%) of O-acetyl-p-nitrosodimethylaniline perchlorate with mp 138° (from glacial acetic acid). IR spectrum: 1772 (=C—$OCOCH_3$), 1628, 1600, 1572, 1080 cm^{-1} (ClO_4^-). Found: C 40.4; H 4.8; Cl 12.2; N 9.5%. $C_{10}H_{13}ClN_2O_6$. Calculated: C 40.9; H 4.4; Cl 12.1; N 9.6%.

N-Acetoxypyridinium perchlorate, with mp 124° (from acetic acid), was similarly obtained in 60% yield. IR spectrum: 1811, 1610, and 1070 cm^{-1}. Found: C 35.4; H 3.4; Cl 14.9; N 5.9%. $C_7H_8ClNO_6$. Calculated C 35.2; H 3.7; Cl 14.8; N 5.8%.

The perchlorates of the o-acetylated derivatives of p-nitrosodimethylaniline and pyridine N-oxide were obtained by alternative synthesis in 55 and 33% yields, respectively, by acylation of the appropriate compounds with acetic anhydride in the presence of molar amounts of 70% perchloric acid (identification by mixed-melting-point measurements).

LITERATURE CITED

1. G. N. Dorofeenko, V. V. Mezheritskii, Yu. I. Ryabukhin, O. V. Ivanova, and L. G. Minyaeva, Khim. Geterotsikl. Soedin., No. 3, 322 (1977).
2. Yu. I. Ryabukhin, V. V. Mezheritskii, and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 4, 460 (1975).

3. T. Irie, E. Kurosawa, and T. Hanada, Nippon Kagaku Zasshi, 79, 1401 (1958); Chem. Abstr., 54, 5657 (1960).

5-ALKOXY-2-VINYLOXAZOLIDINES.

REACTION OF ARENESULFONYL AZIDES WITH METHYL VINYL ETHER IN THE PRESENCE OF α,β-UNSATURATED ALDEHYDES AND KETONES*

V. P. Semenov, I. M. Stroiman,
S. V. Ozernaya, and K. A. Ogloblin

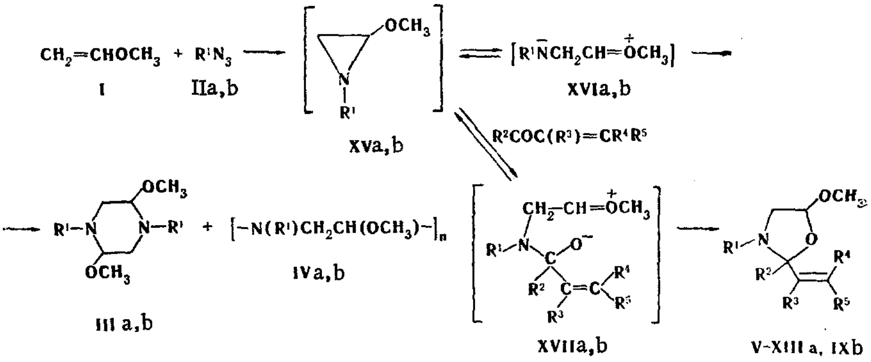
UDC 547.717'77

2-Methyl-1-arylsulfonylaziridines, formed in the reaction of tosyl and p-nitrobenzenesulfonyl azides with methyl vinyl ether, react regiospecifically with α,β-unsaturated aldehydes and ketones to give 5-methoxy-2-vinyl-3-arylsulfonyloxazolidines. The effect of the structure of the aziridines and unsaturated aldehydes and ketones on the stereoselectivity of their reactions is discussed.

2-Alkoxy-1-arylsulfonylaziridines react with aldehydes and ketones to give 5-alkoxy-3-arylsulfonyloxazolidines [1, 3], during which addition to aldehydes proceeds stereospecifically, whereas addition to 2-butanone proceeds stereoselectively to a considerable extent.

The present paper is devoted to the study of the regioselectivity and stereoselectivity of the reaction of α,β-unsaturated aldehydes and ketones with 2-methoxy-1-arylsulfonylaziridines formed as intermediates in the reaction of arenesulfonyl azides with methyl vinyl ether.

The products of the reaction of methyl vinyl ether (I) with tosyl azide (IIa) in the presence of α,β-unsaturated aldehydes and ketones contain 2,5-dimethoxy-1,4-ditosylpiperazine (IIIa), polymer IVa, and substituted 5-methoxy-2-vinyl-3-tosyloxazolidines Va-XIIIa (in 6-53% yields). 5-Methoxy-2-(2-phenylethynyl)-3-tosyloxazolidine (XIVa) was obtained by reaction of ether I, azide IIa, and phenylpropargaldehyde, whereas 5-methoxy-2-(trans-styryl)-3-(p-nitrophenylsulfonyl)oxazolidine (IXb) were obtained by reaction of ether I, p-nitrobenzenesulfonyl azide (IIa), and cinnamaldehyde.



---

*Communication VII of the series "Reaction of organic azides with unsaturated compounds." See [1] for communication VI. The results of this research are protected by an author's certificate [2].

A. A. Zhdanov Leningrad State University, Leningrad 199004. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 332-336, March, 1977. Original article submitted February 2, 1976.