SUBSTITUTED 4(5H)-OXAZOLONES AND THEIR SALTS.

9.* SYNTHESIS OF NEW DERIVATIVES OF 2-[2-(α-HETARYL)ETHENYL]-4(5H)-OXAZOLONIUM PERCHLORATES AND THEIR PROPERTIES

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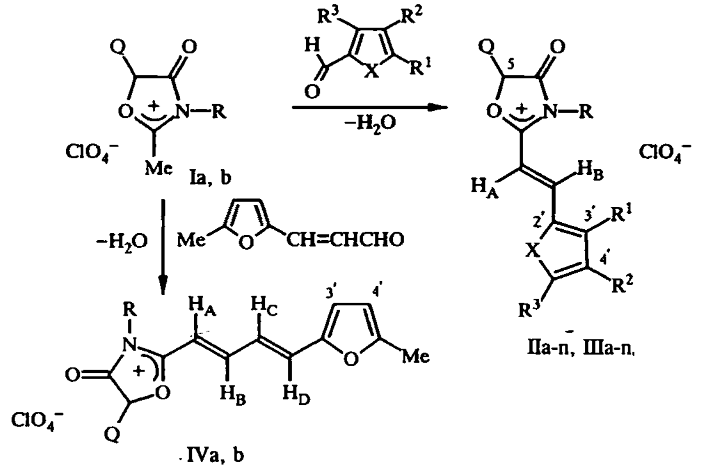
New 2-furyl- and 2-thienylvinyl-4(5H)-oxazolonium perchlorates were synthesized. The action of sodium bicarbonate in 50% aq. ethanol on these salts gave 4(5H)-oxazolones.

2-Methyl-4(5H)-oxazolonium salts (Ia, Ib) were studied as CH-acids in their condensation with carbonyl derivatives of benzene and furan [1, 2]. In the present work, we used aromatic and heteroaromatic aldehydes with substituents at $C_{(2)}$ and $C_{(5)}$ in the cyclic fragment or condensed with benzene or pyrrole rings in this reaction in order to obtain new 4(5H)-oxazolone derivatives, which might hold promise in cyanine dye chemistry as biologically active compounds.



I—IV Q = $MeCOOCH_2CMe_2$; IIa—m, IIIa—*l* X = O; II j-*l*, III m X = S; II m, n, IIIn X = CH = CH; Ia, IIa—n, IVa R = H; Ib, IIIa—n, IVb R = Me; IIa—*l*,n, IIIa—n R^1 = H; IIa—f, IIIa—f R^2 = H, a R^3 = Ph, b R^3 = *p*-MeC_6H_4, c R^3 = *p*-BrC_6H_4, d R^3 = *p*-$NO_2C_6H_4$, e R = *m*-$NO_2C_6H_4$, f R^3 = *o*-NO_2-*p*-ClC_6H_3; IIg R^2, R^3 = CH = CHCH = CH; IIh R^2, R^3 = CH = C(COOEt)NH; IIi R^2, R^3 = CH = C(COOEt)NMe; IIj R^2 = R^3 = H; IIk R^2 = H, R^3 = Cl; II*l* R^2 = H, R^3 = Br, IIm R^1 = R^3 = Cl, R^2 = H; IIn R^2, R^3 = OCH_2O, R^1 = H; IIIg R^2 = H, R^3 = *m*-Cl—*o*-MeC_6H_3O; IIIh R^2 = H, R^3 = *o,p,m*-$Cl_3C_6H_2O$; IIIi R^2, R^3 = CH = CHCH = CH; IIIj R^2, R^3 = CH = C(COOEt)NH; IIIk R^2, R^3 = CH = C(COOEt)NMe; III*l* R^2 = Br, R^3 = I; IIIm R^2, R^3 = H; IIIn R^1 = R^3 = Cl, R^2 = H

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*For Communication 8, see [1].

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TABLE 1. Physical Indices of 4-(5H)-Oxazolonium Perchlorates

Compound	Chemical formula	Found, % Calculated, %				mp, °C	Yield, %
		C	H	Hal	N		
IIa	$C_{21}H_{22}ClNO_9$	54,25 53,91	4,52 4,74	7,76 7,58	3,12 2,99	203...204	73
IIb	$C_{22}H_{24}ClNO_9$	57,86 57,79	4,91 4,98	7,32 7,30	2,82 2,91	198...199	83
IIc	$C_{21}H_{21}BrClNO_9$	46,10 46,14	3,79 3,84	21,02 21,10	2,51 2,56	181...182	74
IId	$C_{21}H_{21}ClN_2O_{11}$	46,12 46,20	4,03 4,10	6,85 6,92	5,41 5,64	190...192	64
IIe	$C_{21}H_{21}ClN_2O_{11}$	46,17 46,20	4,03 4,10	6,88 6,92	5,39 5,46	215...216	56
IIf	$C_{21}H_{20}Cl_2N_2O_{11}$	46,12 46,18	3,60 3,66	12,90 12,98	5,06 5,12	185...186	74
IIg	$C_{19}H_{20}ClNO_9$	50,92 51,67	4,43 4,57	3,36 3,29	8,62 8,34	113...114	81
IIh	$C_{20}H_{23}ClN_2O_{11}$	49,35 49,79	4,88 5,01	6,64 6,80	7,71 7,25	135...136	75
IIi	$C_{21}H_{25}ClN_2O_{11}$	48,36 48,74	4,58 4,80	5,51 5,47	7,03 6,88	125...127	70
IIj	$C_{15}H_{18}ClNO_8S$	44,33 44,18	4,65 4,49	3,71 3,47	9,00 8,74	168...169	60
II*l*	$C_{15}H_{17}BrClNO_8S$	37,11 36,93	3,83 3,79	2,95 2,88	7,97 7,39	155...156	70
IIm	$C_{17}H_{19}Cl_3NO_8$	43,08 43,29	4,17 4,06	2,93 2,97	22,61 22,55	182...183	75
IIn	$C_{18}H_{20}NClO_{10}$	48,60 48,40	4,70 4,40	8,20 7,70	3,70 3,10	184...185	80
IIIa	$C_{22}H_{24}ClNO_9$	54,90 54,83	4,91 5,02	7,72 7,36	2,00 2,91	181...182	81
IIIb	$C_{23}H_{26}ClNO_9$	55,64 55,73	5,16 5,24	7,10 7,15	2,78 2,82	197...198	83
IIIc	$C_{22}H_{23}BrClNO_9$	47,08 47,14	4,05 4,10	20,51 20,57	2,41 2,50	179...180	78
IIId	$C_{22}H_{23}ClN_2O_{11}$	50,11 50,17	4,32 4,37	6,72 6,73	5,43 5,52	185...186	67
IIIe	$C_{22}H_{23}ClN_2O_{11}$	50,11 50,17	4,36 4,37	6,66 6,73	5,48 5,52	212...213	51
IIIf	$C_{22}H_{22}Cl_2N_2O_{11}$	41,01 47,09	3,86 3,92	12,59 12,63	4,90 4,99	192...193	73
IIIg	$C_{23}H_{25}Cl_2NO_{10}$	50,51 49,55	4,63 4,25	13,52 13,00	2,77 2,65	163...164	58
IIIh	$C_{22}H_{21}Cl_4NO_{10}$	43,62 43,95	3,34 3,58	24,15 24,62	2,23 2,31	174...175	56
IIIi	$C_{20}H_{22}ClNO_9$	52,44 52,73	5,00 4,85	8,38 7,81	3,11 3,15	170...172	83
IIIj	$C_{21}H_{25}ClN_2O_{11}$	48,55 48,83	4,25 4,88	7,01 6,83	5,23 5,44	169...170	78
IIIk	$C_{22}H_{27}ClN_2O_{11}$	49,21 49,84	5,21 5,16	7,45 6,72	5,25 5,30	114...116	68
III*l*	$C_{16}H_{18}BrIClNO_9$	31,53 31,47	3,20 2,97	40,00 39,68	2,07 2,29	209...210	84
IIIm	$C_{16}H_{20}ClNO_8S$	38,38 38,30	3,99 4,02	7,00 7,07	2,98 2,79	151...153	71
IIIn	$C_{18}H_{20}Cl_3NO_8$	44,22 44,60	4,13 4,16	21,68 21,94	2,99 2,89	156...157	70
IVa	$C_{18}H_{21}ClNO_9$	49,98 50,18	5,05 4,91	3,66 3,25	8,80 8,23	150...151	50
IVb	$C_{19}H_{23}ClNO_9$	50,23 50,84	5,61 5,16	8,01 7,89	3,03 3,12	157...158	90

The condensation of salts Ia and Ib with aldehydes was carried out with an equimolar reagent ratio in acetic acid or 4:1 glacial acetic acid – acetaldehyde. The reaction conditions and yields of 4(5H)-oxazolonium salts (II-IV) are quite dependent on the structure of the starting reagents. The different synthetic methods are given in the Experimental. The reactions were monitored by thin-layer chromatography. The disappearance of the spot for the corresponding aldehyde in the chromatogram was taken as the end of the reaction.

Salts II-IV are colored crystalline compounds with high melting points, which dissolve well in chloroform, acetone, glacial acetic acid, 1,4-dioxane, and DMSO. The physical indices of these compounds are given in Table 1. As expected from our previous work [2], the condensation of perchlorates Ia and Ib with 5-phenylfurfurals proceeds most smoothly in the case

TABLE 2. Physical Indices of 2-Vinyl-4(5H)-oxazolones

Compound	Chemical formula	Found, % / Calculated, %			mp, °C (ethanol)	R_f[*]	Yield, %
	—	C	H	N			
Va	$C_{21}H_{21}NO_5$	68,73 68,80	5,93 5,97	3,78 3,90	148...150	0,68	96
Vb	$C_{22}H_{23}NO_5$	69,32 69,19	6,15 6,00	3,86 3,70	136...137	0,75	98
Vc[†]	$C_{21}H_{20}BrNO_5$	56,67 56,54	4,52 4,60	3,22 3,09	150...152	0,73	99
Vd	$C_{21}H_{20}N_2O_7$	60,92 61,90	4,93 5,20	6,84 6,98	140...142	0,64	99
Ve	$C_{19}H_{19}NO_5$	66,61 66,92	5,62 5,65	4,86 4,15	149...150	0,45	99
Vf	$C_{20}H_{22}N_2O_7$	59,66 59,70	5,91 5,52	7,46 7,07	147...148	0,30	75
Vg	$C_{21}H_{24}N_2O_7$	59,82 60,61	5,94 5,86	7,05 6,75	143...144	0,40	70
Vh	$C_{15}H_{17}NO_4S$	58,80 58,60	5,80 5,50	4,80 4,60	92...93	0,60	90
Vi[‡]	$C_{15}H_{16}ClNO_4S$	52,25 52,71	4,54 4,71	4,15 4,09	128...130	0,52	95
Vj	$C_{15}H_{16}BrNO_4S$	46,81 46,55	4,42 4,18	4,00 3,61	98...99	0,60	91
Vk	$C_{17}H_{17}Cl_2NO_4$	55,62 55,10	4,82 4,62	3,91 3,86	121...122	0,80	95
V*l*	$C_{18}H_{19}NO_6$	61,00 61,22	5,30 5,73	4,80 4,28	139...140	0,60	80

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[*] Using 20.3 toluene–ethanol eluent, I_2 developer.

[†] Found, %: Br 17.97; calculated, %: Br 18.02.

[‡] Found, %: Cl 10.56; calculated, %: Cl 10.95.

of electron-withdrawing substituents in the benzene ring, leading to shorter reaction time and higher yields of products IIb and IIc and IIIb-IIId. Electron-withdrawing NO_2 substituents diminish the reactivity of aldehydes, as indicated by increased reaction time and decrease in the yields of the condensation products by 11-19 and 10-30%, respectively (Table 1). Products IIIg and IIIh were obtained in low yield and have low solubility in organic solvents such as acetic acid, chloroform, and methylene chloride. Salts IIg-IIi, IIIi-III*l*, IVa, and IVb were obtained in acetic acid at 50-60°C under the conditions described for 5-substituted furan aldehydes [2]. Thiophene aldehydes and substituted benzaldehydes react readily with salts Ia and Ib to give condensation products in high yield under the conditions previously proposed for aromatic aldehydes [2].

The structures of II-V were established by UV, IR, and NMR spectroscopy (Tables 2 and 3).

The electronic spectra of 2-[β-(5-phenylfuryl)vinyl]-4(5H)-oxazolonium salts IIa-IIf and IIIa-IIIf obtained in glacial acetic acid display bands related to $p-\pi$ and $\pi-\pi^*$ electronic transitions. The maximum at 377-509 nm is related to the $\pi-\pi^*$ transition of the major chromophore. The other band at 260-281 nm corresponds to $p-\pi$ and $\pi-\pi^*$ transitions in the phenylfuran and heterocyclic fragments. Analysis of these data indicates a bathochromic shift of the long-wavelength band related to an extension of the conjugation chain in products II and III relative to salts Ia and Ib (λ_{max} 267 and 270 nm). The shift of the *K*-band toward longer wavelengths in salts IIa, IIc-IIe, IIIa, and IIIc-IIIe in comparison to the long-wavelength *K*-band of 2-[β-(aryl)vinyl]-4(5H)-oxazolonium perchlorates [2], which contain analogous substituents (H, Br, and NO_2) in the benzene ring ($\Delta\lambda$ 75-100 and 79-128 nm, respectively, Table 2), indicates that the electronic effects of the substituent in the electron-deficient 4(5H)-oxazolonium cation are better transmitted through a furan ring introduced into the total conjugation system.

Comparison of the electronic absorption spectra of II-IV (Table 3) indicates the existence of various conjugation systems in these structures. The finding that the NH-oxazolonium salts are converted upon dissolution in polar solvents into the corresponding oxazolones, losing a molecule of perchloric acid [2, 3], accounts for the anomalously low value of λ_{max} of the *K*-band in the UV spectra of salts II and IVa in comparison to the corresponding salts III and IVb (Table 3).

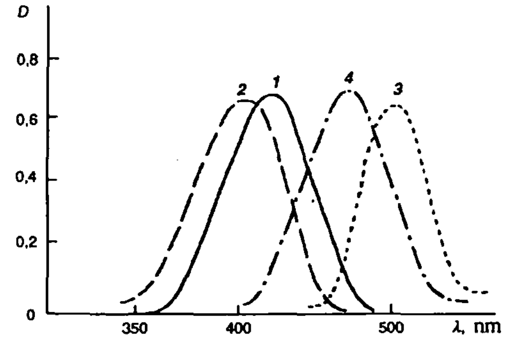
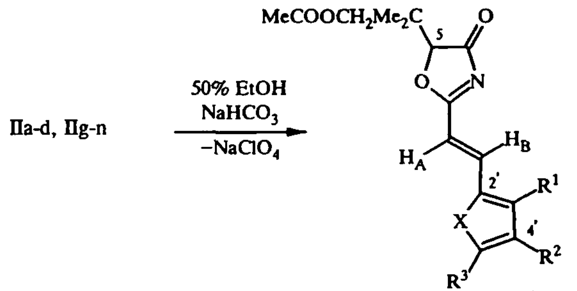


Fig. 1. UV spectra of oxazolones Vc and Vd in glacial acetic acid (curves *1* and *2*) and in a solution of perchloric acid in acetic acid, $C_{HClO_4} = 10^{-2}$ mole/liter (curves *3* and *4*).

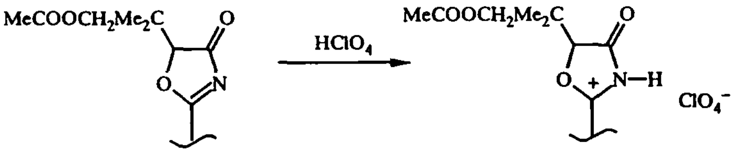
Treatment of solutions of salts IIa-IId with sodium bicarbonate in chloroform or salts IIg-IIn with 50% aqueous ethanol gave the corresponding 4(5H)-oxazolones Va-V*l* in good yield (Table 2).



Va-*l*

Va—g X = O; a—d $R^1 = R^2 = H$, a $R^3 = Ph$, b $R^3 =$ *p*-MeC_6H_4, c $R^3 =$ *p*-BrC_6H_4, d $R^3 =$ *p*-$NO_2C_6H_4$,
e-g $R^1 = H$, e $R^2, R^3 = CH=CHCH=CH$, f $R^2, R^3 = CH—C(COOEt)NH$,
g $R^2, R^3 = CH—C(COOEt)NMe$; Vh-j $X = S, R^1 = R^2 = H$, h $R^3 = H$, i $R^3 = Cl$, j $R^3 = Br$;
Vk,*l* $= CH=CH$, k $R^1 = R^3 = Cl, R^2 = H$; *l* $R^2, R^3 = OCH_2O, R^1 = H$

Deprotonation of salts II is reversible in nature [2, 4]. Protonation at the nitrogen atom and a shift in the equilibrium toward formation of salts IIc and IId occur upon the action of $HClO_4$ in acetic acid on 4(5H)-oxazolones Vc and Vd (see Fig. 1).



Vc,d

IIc,d

This transition is accompanied by a shift in the *K*-band (see Table 3) toward longer wavelengths (λ_{max} 510 and 465 nm, respectively), which is the absorption region of salts IIc and IId determined previously for their solutions in acetic acid containing 10^{-2} mole/liter $HClO_4$ [1].

The IR spectra of these salts show two strong bands related to stretching of the two carbonyl groups. The endocyclic carbonyl group gives rise to the band at 1770-1820 cm^{-1} (shifted toward longer wavelengths in comparison to starting salts Ia and Ib by 10-60 cm^{-1}), while the ester group in the side-chain gives rise to the band at 1720-1740 cm^{-1}, whose frequency depends on the nature of the substituent at $C_{(2)}$ of the heterocycle. The $O-C^+-N$ fragment gives rise to two bands at 1590-1510 cm^{-1}. The band for the endocyclic C=O group in 4(5H)-oxazolones is found at 1720-1750 cm^{-1}, which is also the range for the ester $\nu_{C=O}$ band (Table 3). The stretching vibration bands at 1570-1630 cm^{-1} indicate the presence of C=C and C=N bonds in these molecules.

TABLE 3. IR and UV Spectra of Products

Compound	IR spectrum, ν, cm^{-1}				UV spectrum*	
	C=O	C=C	$O-N^+-O$ (C=N)	C=O ester	λ_{max}, nm	lgε
IIa	1790	1610	1570, 1540	1730	395	4,57
IIb	1780	1590	1530, 1510	1740	266, 420	4,36, 4,67
IIc	1780	1580	1540, 1510	1740	269, 400	3,86, 3,49
IId	1790	1590	1540, 1520	1725	260, 406	3,91, 4,22
IIe	1790	1630	1590, 1570	1740	263, 400	3,54, 4,10
IIf	1780	1570	1540, 1520	1735	262, 393	4,11, 4,48
IIg	1810	1600	1580, 1560	1710, 1730	—	—
IIh	1790	1630, 1610	1590, 1520	1700, 1730	—	—
IIi	1790	1610	1580, 1560	1700, 1720	—	—
IIj	1800	1610, 1580	1590, 1510	1730	357	4,30
IIk	1810	1630	1580, 1510	1740	—	—
II*l*	1800	1610	1590, 1510	1730	364	4,22
IIm	1800	1600	1580, 1510	1720	309	4,19
IIn	1800	1610	1590, 1505	1740	372	4,22
IIIa	1770	1590	1560, 1540	1720	276, 491	3,63, 4,48
IIIb	1780	1580	1550, 1540	1715	281, 509	3,71, 4,12
IIIc	1790	1590	1550, 1545	1720	278, 490	3,83, 4,30
IIId	1795	1600	1550, 1510	1720	250, 377	3,91, 4,97
IIIe	1780	1590	1560, 1510	1725	266, 463	3,85, 4,09
IIIf	1805	1590	1570, 1550	1720	267, 465	3,80, 4,35
IIIg	1815	1610	1550, 1510	1720	—	—
IIIh	1820	1600	1560, 1530	1710	—	—
IIIi	1830	1600	1530, 1510	1735	—	—
IIIj	1790	1610	1590, 1540	1710, 1740	318, 515	3,10, 3,25
IIIk	1790	1610	1590, 1540	1710, 1730	508	2,65
III*l*	1810	1390	1580, 1510	1725	289, 334, 420	3,58, 3,70, 4,08
IIIm	1800	1600	1590, 1550	1720	407	3,55
IIIn	1800	1600	1590, 1510	1720	365	—
IVa	1790	1600, 1580	1590, 1510	1720	402	4,27
IVb	1790	1600	1580, 1510	1720	511	4,67
Va	1720	1610	(1550)	1710	390	4,34
Vb	1745	1630	(1550)	1740	414	4,45
Vc	1725	1615	(1530)	1720	402	4,47
Vd	1720	1630	(1560)	1720	404	4,48
Ve	1750	1630	(1530)	1730	361	4,05
Vf	1730	1610	(1520)	1720, 1700	426	4,68
Vg	1740	1610	(1590)	1730	424	4,43
Vh	1740	1620	(1595)	1730	357	4,42
Vi	1735	1620	(1540)	1710	—	—
Vj	1730	1620	(1540)	1730	364	4,22
Vk	1750	1630	(1545)	1730	309	4,18
V*l*	1740	1600	(1550)	1740	—	—

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*The spectra of salts II-IV were taken in acetic acid, while the spectra of oxazolones V were taken in ethanol.

The PMR spectra for solutions in trifluoroacetic acid confirm the structure of salts IIa-IIn, IIIa-IIIn, IVa, and IVb. The corresponding cations are characterized by a downfield singlet at 4.8-5.1 ppm for the proton at chiral $C_{(5)}$ and an AB quartet with geminal $^2J_{HH} = -11.9$ Hz for the methylene protons, which are anisochronic due to the chirality of $C_{(5)}$ [2]. The protons of the β-CH_2 group in 4(5H)-oxazolones V (Table 4) in CCl_4 are isochronic. In regard to the anisochronicity of these protons in the salts, we may assume that rapid isomerization of salts II and IV on the NMR time scale to dioxanium cation B through intermediate ambident ion A, which gives rise to the 4(5H)-oxazolonium ⇄ cation A equilibrium system, occurs by the action of trifluoroacetic acid [3].

Comparison of the PMR spectra of perchlorates II-IV with the spectrum of 5,5-dimethyl-4-propyl-1,3-dioxanium hexachlorantimonate [5] reveals some similarities in the characteristics of the analogous groups, namely, a downfield shift of the

TABLE 4. PMR Spectra of Products, δ,* ppm, Coupling Constants (*J*), Hz

Compound	Q			5-H	H_A	H_B	3'-,4'-,5'-H^2	R(N$_{(3)}$-Me), R^2, R^3
	Me_2 s, s	MeCO s	CH_2					
1	2	3	4	5	6	7	8	9
IIb	0,85 0,93	1,83	3,82 d 3,95 d $^2J_{HH}$ = –11,9	4,90 s	7,80 d	6,36 d $^3J_{AB}$ = 15,0	7,35 d (1H, 3'-H); 6,90 d (1H, 4'-H); $^3J_{3'4'}$ = 4,0	2,00 s (3H, *p*-Me); 6,90 d (2H); 7,43 d (2H); $^3J_{o,m}$ = 9,0
IIc	0,86 0,90	1,80	3,70 d 3,50 d $^2J_{HH}$ = –11,9	4,90 s	7,83 d	6,40 d $^3J_{AB}$ = 15,0	6,73 d (1H, 4'-H); 7,10 d (1H, 3'-H); $^3J_{3'4'}$ = 4,0	7,13 d (2H$_{Ar}$); 7,30 d (2H$_{Ar}$); $^3J_{o,m}$ = 9,0
IId	0,90 0,97	1,80	3,73 d 3,90 d $^2J_{HH}$ = –11,9	4,93	7,90 d	6,60 d $^3J_{AB}$ = 15,0	6,83 d (1H, 4'-H); 7,20 d (1H, 3'-H) $^3J_{3'4'}$ = 4,0	7,57 d (2H$_{Ar}$); 7,83 d (2H$_{Ar}$); $^3J_{o,m}$ = 9,0
IIe	0,87 0,93	1,80	3,77 d 3,87 d $^2J_{HH}$ = –11,9	4,97	8,13 d	6,60 d $^3J_{AB}$ = 15,0	6,83 d (1H, 4'-H); 7,26 d (1H, 3'-H); $^3J_{3'4'}$ = 4,0	7,10...8,30 m (4H, *o,o,m,p*-H$_{Ar}$)
IIf	0,86 0,93	1,82	3,77 d 3,92 d $^2J_{HH}$ = –11,9	5,00	7,92 d	6,47 d $^3J_{AB}$ = 15,0	6,68 d (1H, 4'-H); 7,03 d (1H, 3'-H); $^3J_{3'4'}$ = 4,0	7,00...7,70 m (3H, *o,m,m*-H$_{Ar}$)
IIh	0,83 0,90	1,80	3,74 d 3,86 d $^2J_{HH}$ = –12	5,08	7,90 d	6,40 d $^3J_{AB}$ = 15,6	7,18 s (1H, 3'-H)	2,60 br. s (1H, NH); 6,48 s (1H, CH); 1,01 t (3H, CH$_3$); 3,02 q (2H, CH$_2$); $^3J_{H,CH3}$ = 7,0
IIi	0,82 0,90	1,80	3,79 d 3,91 d $^2J_{HH}$ = –12	4,90	7,84 d	6,44 d $^3J_{AB}$ = 15,6	7,18 s (1H, 3'-H)	6,62 s (3H, N–Me); 7,20 s (1H, CH); 1,20 t (3H, Me); 4,10 q (2H, CH$_2$); $^3J_{H,CH3}$ = 7,0

TABLE 4 (continued)

1	2	3	4	5	6	7	8	9
IIj	0,83 0,90	1,80	3,89 d 3,76 d $^2J_{HH} = -12$	4,99	6,4 d $^3J_{AB} = 15,6$	8,5 d	6,45 d (1H, 4'-H); 7,55 d (1H, 3'-H); 7,70 d (1H, 5'-H); $^3J_{3'4'} = 4,0$, $^3J_{4'5'} = 4,0$	–
IIk	0,87 0,96	1,83	3,77 d 3,96 d $^2J_{HH} = -12$	5,01 s	8,3 d $^3J_{AB} = 16,00$	6,8 d	7,60 d (1H, 3'-H); 7,40 d (1H, 4'-H); $^3J_{3'4'} = 4,0$	–
IIIa	0,81 0,90	1,80	3,75 d 3,93 d $^2J_{HH} = -11,9$	4,86	7,88 d $^3J_{AB} = 15,0$	6,33 d	7,06 d (1H, 3'-H); 6,83 d (1H, 4'-H); $^3J_{3'4'} = 4,0$	3,10 s (3H, N–Me); 7,15...7,70 (5H, H_{Ar})
IIIb	0,82 0,90	1,82	3,75 d 3,97 d $^2J_{HH} = -11,9$	4,85	7,83 d $^3J_{AB} = 15,0$	6,30 d	7,35 d (1H, 3'-H); 6,78 d (1H, 4'-H); $^3J_{3'4'} = 4,0$	2,02 s (3H, *p*-Me); 3,10 s (3H, N–Me); 6,90 d (2H_{Ar}); 7,43 d (2H_{Ar}); $^3J_{o,m} = 9,0$
IIIc	0,78 0,88	1,80	3,71 d 3,93 d $^2J_{HH} = -11,9$	4,90	7,88 d $^3J_{AB} = 15,0$	6,33 d	7,11 d (1H, 3'-H); 6,73 d (1H, 4'-H); $^3J_{3'4'} = 4,0$	3,10 s (3H, N–Me); 7,15 d (2H_{Ar}); 7,31 d (2H_{Ar}); $^3J_{o,m} = 9,0$
IIId	0,92 1,00	1,87	3,85 d 4,02 d $^2J_{HH} = -11,9$	5,05	8,03 d $^3J_{AB} = 15,0$	6,80 d	7,37 d (1H, 3'-H); 7,03 d (1H, 4'-H); $^3J_{3'4'} = 4,0$	3,20 s (3H, N–Me); 7,65 d (2H_{Ar}); 7,07 d (2H_{Ar}); $^3J_{o,m} = 9,0$
IIIe	0,83 1,00	1,82	3,73 d 3,93 d $^2J_{HH} = -15,0$	4,93	8,22 d $^2J_{AB} = 15,0$	6,53 d	7,33 d (1H, 3'-H); 6,90 d (1H, 4'-H); $^3J_{3'4'} = 4,0$	3,20 s (3H, N–Me); 7,15 d (2H_{Ar}); 7,15...8,33 m (4H, *m,o,o,p*-H_{Ar})
IIIf	0,87 0,93	1,80	3,73 d 3,90 d $^3J_{HH} = -11,9$	4,93	7,9 d $^3J_{AB} = 15,0$	6,43 d	7,13 d (1H, 3'-H); 6,67 d (1H, 4'-H); $^3J_{3'4'} = 4,0$	3,23 s (3H, N–Me); 7,33...7,76 m (3H, *m,m,o*-H_{Ar})
III*l*	0,77 0,88	1,77	3,73 d 3,95 d $^2J_{HH} = -11,9$	5,02	7,90 d $^3J_{AB} = 15,0$	6,58 d	6,97 s (1H, 3'-H)	3,15 s (3H, N–Me)
IVa	0,80 0,90	1,80	3,76 d 3,89 d $^2J_{HH} = -11,5$	4,80	8,00 d. d 6,66 d. d (H_S) $^3J_{AB} = 15,0$; $^3J_{CD} = 15,0$, $^3J_{BC} = 10,0$	7,10 d 5,42 (H_D)	6,90 d (1H, 3'-H); 6,16 d (1H, 4'-H); $^3J_{3'4'} = 4,0$	2,06 s (3H, 5'-Me)

TABLE 4 (continued)

1	2	3	4	5	6	7	8	9
IVb	0,78 0,88	1,80 s	2,88 q $^2J_{HH}$ = −11,5	4,80	8,00 d. d 6,7 d. d (H_S) $^3J_{AB}$ = 15,0; $^3J_{CD}$ = 15,0; $^3J_{BC}$ = 10,0	7,0 d 6,3 d (H_D)	7,01 d (1H, 3'-H); 6,00 d (1H, 4'-H); $^3J_{3'4'}$ = 4,0	2,06 s (3H, 5'-Me); 3,06 s (3H, N–Me)
Vb	0,98 1,13	2,06	4,01	4,50	7,72 d $^3J_{AB}$ = 15,0	6,68 d	6,83 d (1H, 3'-H); 6,71 d (1H, 4'-H); $^3J_{3'4'}$ = 4,0	2,06 s (3H, *p*-Me); 7,19 d (2H$_{Ar}$); 7,63 d (2H$_{Ar}$); $^3J_{o,m}$ = 9,0
Vc	0,95 1,13	2,06	4,00 s	4,48	7,71 d $^3J_{AB}$ = 15,0	6,58 d	6,88 d (1H, 3'-H); 6,75 d (1H, 4'-H); $^3J_{3'4'}$ = 4,0	7,53 s (4H, *o,o,m,m*-H$_{Ar}$)
Ve	0,98 1,06	2,00	3,96 s	4,50	7,78 d $^3J_{AB}$ = 15,6	6,85 d	7,01 s (1H, 3'-H)	7,38 m (4H, C_4H_4)
Vf	0,90 1,10	2,00	3,96 s	4,50	7,70 d $^3J_{AB}$ = 15,6	6,63 d	6,85 s (1H, 3'-H)	2,70 br. s (1H, NH); 6,66 s (1H, CH); 1,30 t (3H, CH_3); 4,36 q (2H, CH_2); $^3J_{HCH3}$ = 7,0
Vg	0,95 1,08	2,03	3,90 s	4,50	7,70 d $^3J_{AB}$ = 15,6	6,68 d	6,76 s (1H, 3'-H)	2,70 s (1H, N–Me); 6,60 s (1H, CH); 1,28 t (3H, CH_3); 4,40 q (2H, CH_2); $^3J_{HCH3}$ = 7,0
Vh	0,96 1,13	2,00	3,98 s	4,48	8,08 d $^3J_{AB}$ = 15,6	6,50 d	7,30 d (1H, 3'-H); 7,00 d (1H, 4'-H); 7,40 (1H, 5'-H)	—
Vj	0,94 1,10	2,00	3,98 s	4,46	7,90 d $^3J_{AB}$ = 15,6	6,39 d	7,08 d (1H, 3'-H); 6,86 d (1H, 4'-H); $^3J_{3'4'}$ = 4,0	—
Vk	0,98 1,08	1,96	3,96 s	4,53	8,02 d $^3J_{AB}$ = 15,6	6,65 d	—	7,00...7,70 m (3H, *o,m,m*-*H*$_{Ar}$)
V*l*	1,02 1,13	2,05	4,00 s	4,36	7,79 d $^3J_{AB}$ = 15,6	6,52 d	6,29-(3',6'-,7'-H)	6,04 s (2H, CH_2O); 6,92 m

*Spectra for IIb-IIh, IIIa-IIIf, and III*l* taken in CF_3CO_2D, spectra for IIi-IIk, IVa, and IVb taken in CF_3CO_2H, for Vb, Vc, Ve, Vh, and Vj taken in $CDCl_3$, for Ve-Vg, Vk, and V*l* taken in CD_2Cl_2.

*2For V*l*, also signals for 6'- and 7'-H.

TABLE 5. Mass Spectra of 4(5H)-Oxazolones V

Compound	m/z (I_{rel}, %)*
Vb	381 (21,7), 308 (14,9), 266 (11,7), 225 (67,2), 209 (100), 129 (21,3), 113 (21,86), 95 (15,4), 83 (18,0), 44 (42,4), 32 (36,9)
Vc*2	447 (10,8), 374 (7,9), 232 (9,2), 291 (44,0), 289 (34,9), 275 (71,9), 195 (13,3), 113 (52,2), 95 (31,9), 83 (31,3), 44 (100)
Vd	412 (18,4), 339 (13,5), 297 (8,2), 256 (78,3), 240 (96,7), 210 (19,2), 194 (12,2), 182 (11,5), 113 (49,3), 44 (64,3), 28 (100)
Ve	341 (10,8), 268 (5,8), 226 (9,4), 198 (1,3), 185 (44,8), 171 (21,2), 169 (100), 143 (2,7), 141 (2,2), 140 (12,6), 115 (12,7), 89 (2,23), 43 (38,7)
Vk*3	369 (1,3), 296 (2,2), 255 (7,3), 254 (1,1), 213 (1,06), 199 (62,9), 197 (19,0), 171 (7,7), 145 (3,4), 136 (12,66), 109 (2,1), 73 (2,2), 43 (100)

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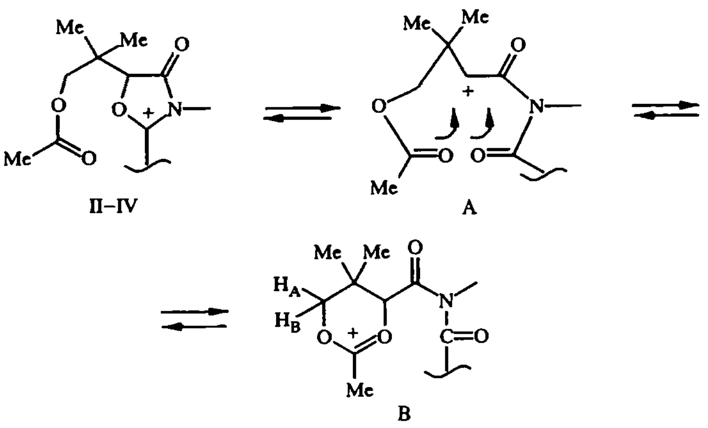
*The peaks for M^+ and the 10 strongest ions are given.

*2Molecular ion m/z values calculated for the ^{81}Br isotope.

*3Molecular ion m/z values calculated for the ^{35}Cl isotope.

lines for 4-H (δ 5.36 ppm) and AB quartet splitting ($^2J_{HH}$ = 11.0 Hz) for H_A and H_B at $C_{(6)}$ in the ring (δ_{H_A} 4.94, δ_{H_B} 5.08 ppm). The PMR signals for 5-CH and β-CH_2 may thus be assigned to the protons at $C_{(5)}$ and $C_{(6)}$, whose chemical shifts are typical for 1,3-dioxanium cation B.



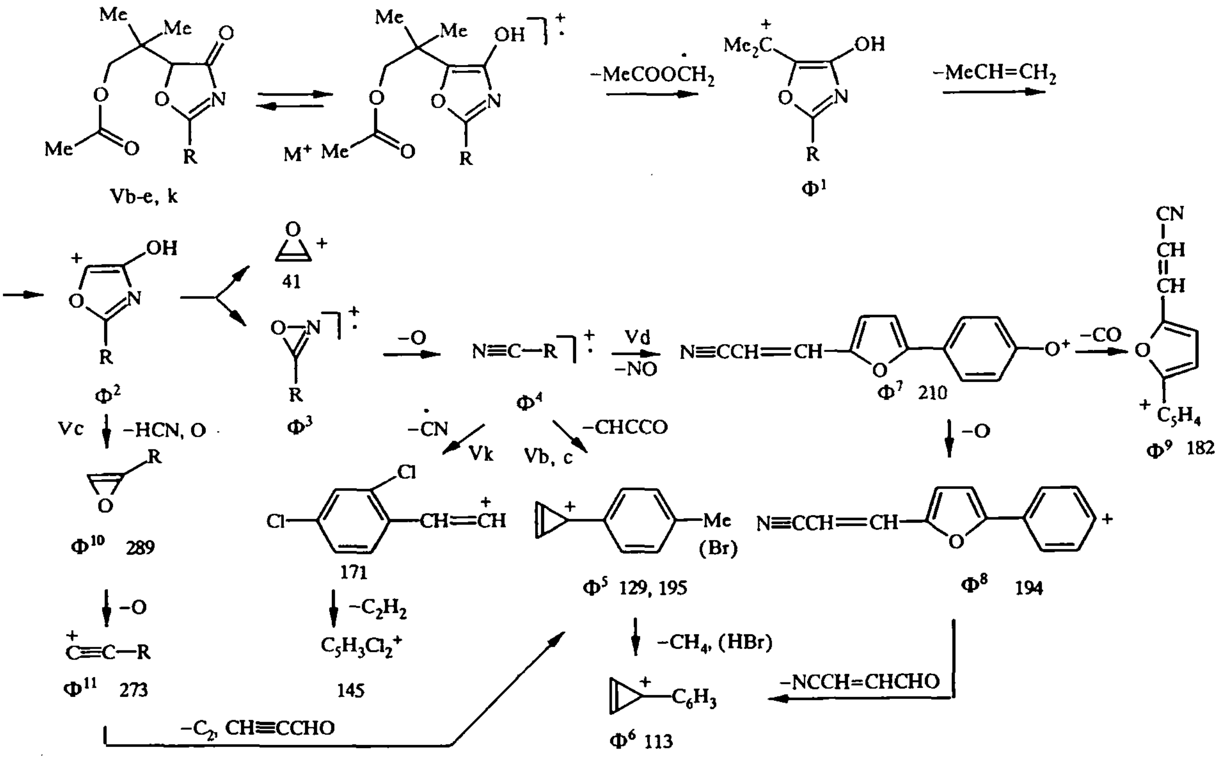
II-IV

A

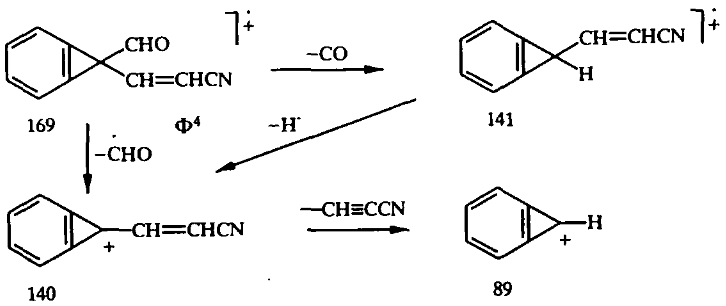
B

The chemical shifts of the olefinic protons both in salts II-IV and oxazolones V are 6.3-8.5 ppm. These signals appear as AB quartets with vicinal coupling $^3J_{AB}$ = 15-16 Hz (Table 4), indicating *trans* arrangement relative to the double bond. The coupling constants for the ABCD protons in salts IVa and IVb indicate that the olefinic bond system has *s,trans-E,E* configuration. The orientation of the furan ring relative to the conjugated system was not determined since the long-range coupling constant between olefinic proton H_D and 4-H in the furan ring could not be found. The resonance signal for the NH group in the spectra of salts IIa-IIn and IVa did not appear due to exchange with traces of water in the trifluoroacetic acid used as the solvent [2].

Analysis of the mass spectra of 2-vinyloxazolones Vb-Ve and Vk showed molecular ion peaks M^+ for all the samples studied, corresponding to the calculated values (Table 5) and their dissociative ionization may be represented by the general scheme given below. Comparison with previous data [3, 6] indicates that the step prior to decomposition of the molecular ion involves enolization through tautomeric transfer of a hydrogen atom from $C_{(5)}$ in the ring to the endocyclic carbonyl oxygen atom to give 4-hydroxyoxazole derivatives [7, p. 111]. The electron impact decomposition of the molecular radical-ions begins in all cases with the characteristic group attached to $C_{(5)}$ in the oxazole ring and, then, the heterocycle itself to give characteristic ions and radical-cations $\Phi^1-\Phi^4$. Transformation of the furan heterocycle begins only after complete decomposition of this group. However, the phenylfurylethenyl fragment containing the NO_2 group remains unaltered until rather advanced stages of the fragmentation (decomposition $\Phi^4 \rightarrow \Phi^7 \rightarrow \Phi^8$ and $\Phi^7 \rightarrow \Phi^9$), consecutively losing NO, O, and CO [7]. The subsequent fragmentation of radical-cation Φ^4 of phenylfurylvinyloxazolones Vb-Vd proceeds analogously to the furan



derivative to give a stable ion with *m/z* 113 (Φ^6) [7]. The characteristic initial decomposition for oxazoles with loss of a hydrocyanic acid molecule [7, 8] was determined in the case of Vc for cation Φ^2 with subsequent elimination of oxygen and carbon atoms and an acrolein molecule in the decomposition chain $\Phi^2 \rightarrow \Phi^{10} \rightarrow \Phi^{11} \rightarrow \Phi^5$. Benzofurylvinyl-4(5H)-oxazolone Vd decomposes starting with radical-cation Φ^4, as established previously for substituted benzofurans, in which, not excluding the loss of CHO˙, the consecutive loss of CO and H˙ occurs [7, 9].



EXPERIMENTAL

The IR spectra were taken on a Specord-71 spectrometer at room temperature in Vaseline mulls at 400-4000 cm^{-1}. The electronic spectra at 250-800 nm were taken on Specord UV and Specord M-40 spectrophotometers for solutions in glacial acetic acid. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz with HMDS as the internal standard. The mass spectra were taken on Varian MAT-311A and Hitachi M-80B spectrometers by direct inlet into the ion source at 200, 140, 100, and 50°C. The ionizing electron energy was 70 eV.

Perchlorates Ia and Ib were obtained according to Potts [6], while the substituted furfurals were described by various workers [11-13]. The solutions of $HClO_4$ in acetic acid were prepared according to a reported method [14].

2-{2-[5-(4-Nitrophenyl)-2-furyl]ethenyl}-5-(1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolonium Perchlorate (IId). A sample of 1.086 g (0.005 mole) 5-(4-nitrophenyl)furfural was added to a mixture of 1.57 g (0.005 mole) perchlorate Ia in 4 ml glacial acetic acid, followed by the dropwise addition of 2 ml acetic anhydride. The mixture was maintained on a water bath at 60°C for 4 h and then at room temperature for 2 h. The precipitate formed after cooling of the reaction mixture was filtered off and washed with 1:3 ethyl acetate—ether and then, ether to give 1.53 g (64%) IId. Analogous procedures with variation of the reaction temperature and time gave salts IIa (20-25°C, 15-20 min), IIb (20-25°C, 15-20 min), IIc and IIf (60°C, 3-7 min), IIe (60°C, 3 h), and IIk-IIn (60°C, 1 h).

2-[2-(Benzo[*b*]furyl-2)ethenyl-1]-5-(1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolonium (IIg). A sample of 0.6 g (0.005 mole) benzofurfural was added to a mixture of 1.57 g (0.005 mole) perchlorate Ia in 3 ml glacial acetic acid and maintained on a water bath at 50-60°C for 30 min. A crystalline precipitate formed after cooling and further precipitate was formed by adding ether. The precipitate was filtered off and washed with ether to give 1.3 g (83%) IIg. Analogous procedures with maintenance of the reaction mixture at 60°C for 60 min gave IIh-IIi, IIIg-III*l*, IVa, and IVb.

2-{2-[5-(4-Nitrophenyl)furyl-2]ethenyl}-3-methyl-5-(1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolonium Perchlorate (IIId). A sample of 1.08 g (0.005 mole) 5-(4-nitrophenyl)furfural was added to a mixture of 1.71 g (0.005 mole) 2,3-dimethyl-5-(1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolonium perchlorate Ib in 4 ml glacial acetic acid and, then, 1 ml acetic anhydride was slowly added dropwise. The mixture was maintained on a water bath at 60°C for 2.5-3 h. The precipitate formed after cooling was treated as described for salt IId to give 1.74 g (67%) IIId. Analogous procedures varying the reaction temperature and heating time gave salts IIIa and IIIb (20-25°C, 10-15 min), IIIc and IIIf (60°C, 3-5 min), IIIe (60°C, 2-2.5 h), IIIm, IIIn, and IVb (60°C, 1-1.5 h).

2-{2-[5(Phenyl)furyl-2]ethenyl}-5-(1,1-dimethyl-2-acetoxyethyl-4(5H)-oxazolone (Va). A sample of 3 g (0.036 mole) sodium bicarbonate was added to a suspension of 4.68 g (0.01 mole) perchlorate IIa in 25 ml chloroform. A sample of 0.005 mole water was added dropwise with stirring. The reaction mixture was maintained at room temperature for 20 min. The precipitate was filtered off. The mother liquor was washed with water until the wash water was neutral and dried over anhydrous sodium sulfate. The solvent was distilled off to give 3.52 g (96%) crystalline 4(5H)-oxazolone Va.

Oxazolones Vb-Vd were obtained analogously.

2-[β-(2,3-Benzofuryl-5)vinyl]-5-(1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolone (Ve). A sample of 2 g (0.005 mole) perchlorate IIg was dissolved in 5 ml 50% aqueous ethanol. The crystalline precipitate formed after 5-10 min was filtered off and washed with water to give 1.49 g (99%) Ve. Oxazolones Vf-V*l* were prepared analogously.

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