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5-ALKOXY-2-VINYLOXAZOLIDINES. REACTION OF ARENESULFONYL AZIDES WITH METHYL VINYL ETHER IN THE PRESENCE OF α,β-UNSATURATED ALDEHYDES AND KETONES*

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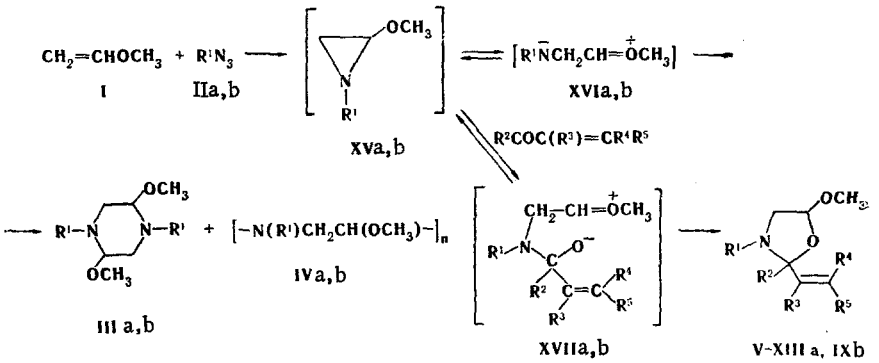
2-Methyl-1-arylsulfonylaziridines, formed in the reaction of tosyl and p-nitrobenzenesulfonyl azides with methyl vinyl ether, react regiospecifically with α,β-unsaturated aldehydes and ketones to give 5-methoxy-2-vinyl-3-arylsulfonyloxazolidines. The effect of the structure of the aziridines and unsaturated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

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IIa—XIIIa R^1=Ts; IIb—IVb, IXb, XVIb—XVIIIb R^1=*p*-$O_2NC_6H_4SO_2$; Va R^2=R^3=R^4=R^5=H; VIa R^2=R^4=R^5=H, R^3=CH_3; VIIa R^2=R^4=R^5=H, R^3=$(CH_3)_2CH$; VIIIa R^2=R^3=R^4=H, R^5=CH_3; IXa,b R^2=R^3=R^4=H, R^5=C_6H_5; Xa R^2=R^3=R^4=H, R^5=3-ClC_6H_4; XIa R^2=R^4=H, R^3=Br, R^5=C_6H_5; XIIa R^3=H, R^2=R^4=R^5=CH_3; XIIIa R^2=CH_3, R^3=R^4=H, R^5=C_6H_5

As a rule the oxazolidines are formed in good yields, higher than the yields in the reactions of 2-methoxy-1-arysulfonylaziridines (XVa,b) with saturated aldehydes and ketones [1-3]. The low yields of the simplest oxazolidines Va and VIa are associated with polymerization of acrolein and methacrolein under the reaction conditions. Since the reactivities of α,β-unsaturated carbonyl compounds with respect to nucleophilic reagents are lower than the reactivities of the corresponding saturated compounds, the increase in the percentage of vinyloxazolidines in the reaction mixture can be explained by a decrease in the rate of the reverse conversion of XVII to XVI.

According to the PMR spectra data (Table 1), the reaction mixtures do not contain products of (3 + 2) addition of aziridine to the C=C bond of unsaturated aldehydes and ketones and products formally corresponding to (3 + 4) cycloaddition of aziridine XV to the system of C=C—C=O bonds. The IR spectra (Table 2) of the individual oxazolidines at 500-700 cm^{-1} are analogous to the spectra of the previously obtained 5-alkoxy-3-tosyloxazolidines [1, 3]. The IR spectra confirm the presence of a C=C bond in the 2-vinyloxazolidines and a C=C bond in oxazolidine XIVa; the characteristic absorption bands of a carbonyl group were absent in all cases. The data from the IR spectra of oxazolidines IXa,b and XI, obtained from aromatic carbonyl compounds, are in complete agreement with the data for 2-aryloxazolidines [4]. The PMR spectra of the oxazolidines confirm the presence of an unsaturated $R^5R^4C = C(R^3)-$ fragment, and the characteristics of the ring protons of the oxazolidine ring are the same as those observed for the previously synthesized oxazolidines [1-3].

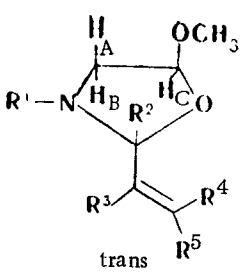
Cinnamaldehyde and a polymer are formed in the hydrolysis of oxazolidine IXa with refluxing dilute sulfuric acid; this is in agreement with data on the solvolysis of 2-alkoxy-3-tosyloxazolidines [3].

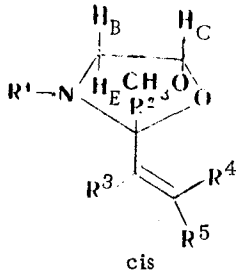
In almost all cases (Table 1) the oxazolidines are obtained as mixture of cis and trans isomers. The assignments of the signals in the PMR spectra to isomeric oxazolidines was made from the data in [1, 3]. As a rule, the 4-H protons of the cis-oxazolidines had very close chemical shifts (a difference of no more than 0.1 ppm) at 3.4-3.6 ppm and very small spin—spin splitting constants (see Fig. 1). The geminal $J_{H_AH_B}$ constants for the cis-oxazolidines therefore do not lend themselves to determination, and the vicinal $J_{H_AH_B}$ and $J_{H_BH_C}$ constants of these oxazolidines were determined approximately. For similar reasons, the accurate determination and assignment of the shifts of the 4-H protons for the cis-oxazolidines are not possible. The presence of two protons of the AB proton of the ABX ring system of cis-oxazolidine IXa at 3.4-3.6 ppm was confirmed by the superimposition of a second frequency on this multiplet, as a result of which the quartet of the 5-H proton of the cis-oxazolidine was converted to a singlet. The most nearly complete assignment of all of the lines of the spectrum (with allowance for the above reservations) was found to be possible for oxazolidine IXa (see Fig. 1). We were able to confirm the correctness of this assignment of the signals in the case of oxazolidine XIa, the individual trans isomer of which we were able to isolate from the mixture of isomers by recrystallization.

Oxazolidines Va-VIIa, which contain a large percentage of the trans isomers, like trans-5-methoxy-2-alkyl-3-tosyloxazolidines, absorb at 1240-1250 cm^{-1}, whereas the remaining 2-vinyloxazolidines have two bands in their IR spectra — a more intense band at 1230-1250 cm^{-1} (trans isomer) and a less intense band at 1260-1280 cm^{-1} (cis isomer). Similarly, there are two bands of equal intensity at 1235-1240 and 1255-1260 cm^{-1} in the IR spectra of 5-methoxy-2,2-dimethyl-3-arylsulfonyloxazolidines.

The percentages of the cis-oxazolidines were determined from the area of the 2-H signal, whereas the percentages of the cis isomer in the case of Va-i were determined from the areas of the signals of 2-CH_3 groups; in individual cases the areas of the 4-H signals and the signals of the vinyl substituent were used to calculate the percentages of the cis isomers. The percentage of the cis isomers in 2-(1-R-vinyl)oxazolidines Va-VIIa decrease as the volume of the substituent increases: 24% (R = H), 19% (R = CH_3), and 0% (R = iso-C_3H_7), in agreement with the data in [3]. On the whole, the percentages of the cis isomers are higher for the

TABLE 1. PMR Spectra of Oxazolidines





(Va—XIVa, R^1 = Ts; IXb, R^2 = p-$O_2NC_6H_4SO_2$)

Compound	R^2	R^3	R^4	R^5	Percentage of the cis isomer, %	Isomer	Chemical shifts, δ, ppm								Spin–spin split. const., Hz*					Solvent
							H_A	H_B	H_C	OCH_3	R^2	R^3	R^4	R^5	H_BH_C	H_AH_C	H_AH_B	R^2R^3	R^3R^4	
Va	H	H	H	H	24±3	trans	3,18	3,67	4,65	3,24	5,63	5,86	5,36	5,16	5,2	3,3	12,1	6	16	CCl_4
						cis	3,44	3,42	4,91	2,97			5,41	5,19	2,5	2,3			16	
VIa	H	CH_3	H	H	19±2	trans	3,12	3,72	4,48	3,24	5,53	1,76	5,17	4,90	5,4	4,6	12,8			CCl_4
						cis	3,47	3,44	4,48	2,99		1,68	5,12	4,96	3,2	1,7				
VIIa	H	i-C_3H_7	H	H	—	trans	3,04	3,72	4,36	3,23	5,71	1,08 2,47	4,93	5,24	5,4	5,1	13,2			CCl_4
VIIIa	H	H	H	CH_3	7,5±1,5	trans	3,19	3,64	4,48	3,23	5,54	5,50	5,77	1,69	5,5	3,3	12,0	6,2	14,0	CCl_4
						cis	3,44	3,41	4,88	3,00					3	2				
IXa	H	H	H	C_6H_5	40±2	trans	3,39	3,76	4,81	3,29	5,88	6,14	6,69	7,30	5,4	3,0	11,8	6,4	15,6	$CHCl_3$
						cis	3,60	3,56	5,03	3,07	5,56	6,07	6,75		3,0	2,1	12	6,1	15,8	
IXb	H	H	H	C_6H_5	19±4	trans	3,63	3,98	5,07	3,30	6,08	6,30	6,82		5,1	2,6	11,6	6,7	15,6	$C_6H_5NO_2$
						cis	3,77	3,74	5,11	2,98	5,79	6,28	6,76		3	2		6,4	13,1	
Xa	H	H	H	m-ClC_6H_4	15±1	trans	3,58	3,89	4,90	3,27	5,99	6,29	6,69		5,2	2,7	11,9	6,0	15,6	$C_6H_5NO_2$
						cis	3,73	3,70	5,13	3,03	5,69	6,28	6,75		3,4	1,9		6,0	15,5	
XIa	H	Br	H	C_6H_5	20±2	trans	3,39	3,88	4,82	3,36	5,94				5,1	4,4	12,5			$CHCl_3$
						cis	3,75	3,71	5,11	3,18	5,72									
XIIa	CH_3	H	CH_3	CH_3	33±3	trans	3,23	3,59	4,94	3,20	1,61	5,41	1,67	1,67	5,3	2,4	10,3			CCl_4
						cis	3,49	3,46	4,96	3,28	1,67	5,30	1,61	1,61	3,5	3,5	9,5			
XIIIa	CH_3	H	H	C_6H_5	48,5±1,5	trans	3,51	3,86	5,14	3,38	1,88	6,15	6,64		5,0	2,5	10,2		16,0	$CHCl_3$
						cis	3,64	3,60	5,2	3,32	1,84	6,07	6,72						16,0	
XIVa	H	$C\equiv C-C_6H_5$†			20±3	trans	3,34	3,77	4,80	3,31	6,06				5,2	3,0	12,1			CCl_4
						cis	3,53	3,50	5,04	3,08	5,83				2,5	2				

*For oxazolidine V, $J_{R^3R^5}$ = 10 Hz and $J_{R^4R^5}$ = 2 Hz; for oxazolidine VI, $J_{R^4R^5}$ = 1.5 Hz; for oxazolidine VIII, $J_{R^4R^5}$ = 6.0 Hz.

†This is the substituent in the 2 position of the oxazolidine.

TABLE 2. Characteristics of the Oxazolidines*

Compounds	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	N	S		C	H	N	S	
Va	85.0—85.6	55.0 54.9	6.0 6.2	4.6 4.6	11.4 11.2	$C_{13}H_{17}NO_4S$	55.1	6.0	4.9	11.3	12†
VIa	78.5—79	56.4 56.5	6.5 6.5	4.3 4.5	10.8 10.9	$C_{14}H_{19}NO_4S$	56.5	6.4	4.7	10.8	6†
VIIa	75.5—76‡	58.7 58.9	6.9 7.1	3.9 4.0	9.9 9.7	$C_{16}H_{23}NO_4S$	59.1	7.1	4.3	9.9	53†
VIIIa	83.5—84	56.0 55.9	6.5 6.6	4.5 4.6	11.0 11.0	$C_{14}H_{19}NO_4S$	56.5	6.4	4.7	10.8	40
IXa	122.5—123	63.7 63.5	6.0 6.0	3.8 3.9	9.1 9.1	$C_{19}H_{21}NO_4S$	63.5	5.9	3.9	8.9	28
IXb	145—145.5	55.5 55.6	4.6 4.6	6.8 6.8	7.8 7.7	$C_{18}H_{18}N_2O_6S$	55.4	4.7	7.2	8.2	64
XIa	139.5—140‡	51.9 51.9	4.8 4.7	2.8 2.9	7.1 7.1	$C_{19}H_{20}BrNO_4S$	52.1	4.6	3.2	7.3	49
XIVa	108—111	63.3 63.9	5.6 5.4	3.6 3.5	9.0 9.2	$C_{19}H_{19}NO_3S$	63.8	5.4	3.9	9.0	33

*We were unable to isolate analytically pure samples of X, XII, and XIII; X, XII, and XIII were obtained in 18, 21, and 23% yields, respectively, as viscous colorless oils.
†In addition to oxazolidines V-VII, piperazine IIIa was isolated in 17, 31, and 29% yields, respectively.
‡ The melting points of the individual trans isomers are presented.

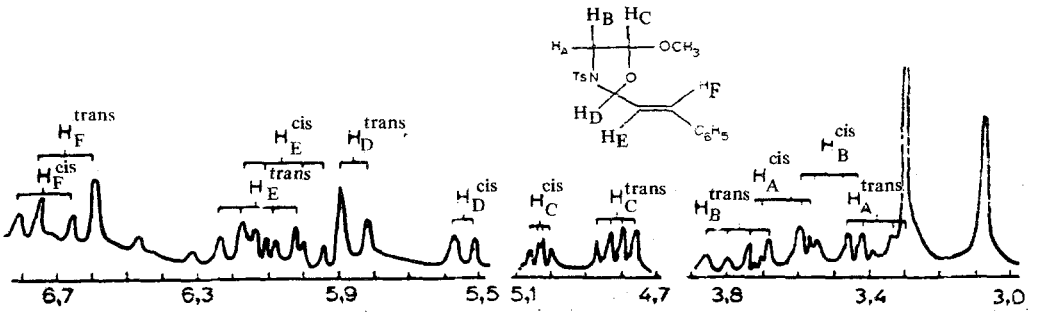
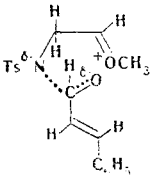


Fig. 1. PMR spectrum of 5-methoxy-2-trans-styryl-3-tosyloxazolidine (IXa) in chloroform.

vinyloxazolidines than for the 2-alkyloxazolidines, and they are particularly high for 2-styryloxazolidine IXa (40%). The explanation for this may be given from the position of the decrease in the energy of the transition state between dipolar ions XVI and XVII in the case of a cisoid orientation of the vinyl and oxonium substituents.



Whereas methyl benzyl ketone undergoes 90% addition to aziridine XVa in such a way that the benzyl substituent becomes trans-oriented with respect to the methoxy group [3], in the case of methyl styryl ketone the percentage of oxazolidine XIIIa with a trans orientation of the styryl substituent and the methoxy group amounts to only 50%. The percentage of the cis isomer in the case of oxazolidine XIIa is very high. Thus the trans-stereoselectivity of the addition of styrylcarbonyl compounds is less than that of saturated carbonyl compounds. A decrease in the nucleophilicity of nitrogen in dipolar ion XVIIb as compared with ion XVIIa leads to an increase in the stereoselectivity of the addition to cinnamaldehyde (the percentage of the cis isomer amounts to 40% in the case of oxazolidine IXa and 19% in the case of oxazolidine IXb). On the other hand, a decrease in the nucleophilicity of the C=C bond of an unsaturated aromatic aldehyde also leads to an increase in the trans-stereoselectivity of the addition of dipolar ion XVIa: 40% of the cis isomer in the case of 2-styryloxazolidine

IXa and 15-20% of the cis isomers in the case of 2-styryloxazolidines Xa and XIa, which contain electron-acceptor substituents. Similarly, higher stereoselectivity of the addition of aziridine XVa to 3-phenyl-2-propyn-1-al is observed (20% of the cis isomer).

EXPERIMENTAL

The PMR spectra of the compounds were recorded with a Varian-HA-100 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of mineral oil suspension of the compounds were recorded with a UR-20 spectrometer. Preparative thin-layer chromatography (TLC) was carried out on LS_{254} 5/40 silica gel with a luminescent indicator and elution with petroleum ether (or hexane)—acetone (3:1).

The 2-bromo-3-phenyl-2-propen-1-al, with mp 72.5-73.5° (from ethanol), contained only one of the isomers, according to the PMR spectral data: δ 7.34 m (2H), 7.39 s (1H), 7.79-7.93 m (3H), and 9.19 s (1H).

trans-3-(m-Chlorophenyl)-2-propen-1-al. A 2% alcohol solution of sodium hydroxide was added dropwise to a mixture of 7 g of m-chlorobenzaldehyde and 8.8 ml of acetaldehyde at 0-5° until the mixture had pH 9. After stirring for 30 min, the excess acetaldehyde was evaporated, and 5 g of acetic anhydride was added with stirring. After 2 h, the mixture was poured into 2% hydrochloric acid, and the acid mixture was extracted with ether. The ether was evaporated, and the residual yellow oil was vacuum distilled to give 4 g (45%) of m-chlorocinnamaldehyde with mp 45° and bp 132° (7 mm). IR spectrum (CCl_4) 2830, 2740, 1706 (CHO), 3010, 1645, and 980 cm^{-1} (trans-CH=CH). PMR spectrum (CCl_4), δ: 6.60 (dd, 1H, J_{vic} = 7.5 Hz, J_{trans} = 16.0 Hz), 7.28 (d, 1H, J = 16.0 Hz), 7.31 (m, 3H), 7.48 (s, 1H), and 9.60 ppm (d, 1H, J = 7.5 Hz). Found: C 61.7; H 4.3%. C_9H_7ClO. Calculated: C 61.9; H 4.2%.

3-Phenyl-2-propyn-1-al was obtained in 59% yield from 2-bromo-3-phenyl-2-propenal and had bp 101-104° (10 mm) and n_D^{17} 1.6058.

5-Methoxy-2-vinyl-3-arylsulfonyloxazolidines Va-XIVa and IXb. These compounds were obtained by the method in [1] by heating 2 mmole of the azide, 6 mmole of the ether I, and 6 mmole of the carbonyl compound at 40° for 2 h in a sealed tube. Oxazolidines Va-VIIa, IXa-XIVa, and IXb were isolated from the reaction mixture by preparative TLC. The percentages of the cis and trans isomers (Table 1) were determined from the PMR spectra after isolation of the mixture by means of TLC, and the analytically pure preparations (Table 2) were obtained by two recrystallizations from hexane or from hexane—chloroform (10:1). Except for oxazolidine XIa, the oxazolidines could not be separated either by TLC or recrystallization. Oxazolidine VIIIa was isolated by repeated treatment of the reaction mixture with boiling hexane (as described in [3]), evaporation of the mother liquors, and two recrystallizations from hexane. Oxazolidines IXa,b were similarly isolated in 26 and 19% yields, respectively, during which poly(2-methoxy-1-tosylaziridine) IVa was isolated in 36 and 49% yields along with oxazolidines VIIIa and IXa.

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