REACTION OF ARENESULFONYL AZIDES WITH ALKYL VINYL ETHERS IN THE PRESENCE OF KETONES. 5-ALKOXY-3-ARYLSULFONYLOXAZOLIDINES*

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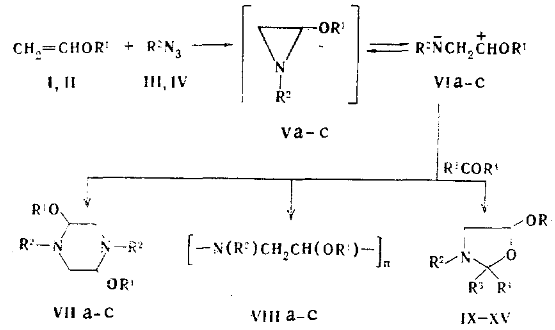
2-Methoxy- and 2-ethoxy-1-arylsulfonylaziridines, which are formed by reaction of arenesulfonyl azides with methyl and ethyl vinyl ethers, react with ketones to give 5-alkoxy-2,2-dialkyl-3-arylsulfonyloxazolidines, along with products of dimerization and polymerization of the alkoxyaziridines.

It is known that 1-arylsulfonylaziridines add to chloral under nucleophilic catalysis conditions to give 2-trichloromethyl-1-arylsulfonyloxazolidines; C-substituted-1-arylsulfonylaziridines could not be made to undergo ring expansion [3].

The present paper is devoted to the study of the reaction of ketones with 2-alkoxy-1-arylsulfonylaziridines, the formation of which, as intermediates in the reaction of arenesulfonyl azides with vinyl ethers, has been previously demonstrated [4].

Methyl and ethyl vinyl ethers (I, II) react with tosyl azide (III) and ether I reacts with p-nitrobenzenesulfonyl azide (IV) in the presence of acetone at 40°C to give products of (3 + 2)-cycloaddition at the carbonyl group of acetone – 2-alkoxy-1-arylsulfonylaziridines (V). In addition to the oxazolidines, dimers and polymers of the aziridines or the corresponding dipolar ions VI – 2,5-dialkoxy-1,4-bis(arylsulfonyl)piperazines (VII) and poly-2-alkoxy-1-arylsulfonylaziridines) (VIII) – were isolated. Oxazolidines IX-XI were obtained in 30-40% yields.

According to the data from thin-layer chromatography (TLC) and the PMR spectra, the reaction mixtures contain small amounts of alkyl N-arylsulfonylacetimidates and alkyl N-arylsulfonylformimidates, which are side products of the conversion of 5-alkoxy-1-arylsulfonyl-Δ^2-1,2,3-triazolines to alkoxyaziridines V [4].



I $R^1=CH_3$; II $R^1=C_2H_5$; III $R^2=Ts$; IV $R^2=O_2NC_6H_4SO_2$; Va–VIIIa $R^1=CH_3$, $R^2=Ts$;
Vb–VIIIb $R^1=C_2H_5$, $R^2=Ts$; Vc–VIIIc $R^1=CH_3$, $R^2=p\text{-}O_2NC_6H_4SO_2$

The cyclic structure of oxazolidines IX-XI was confirmed by the following data from the PMR spectra (Table 1): the nonequivalence of the two methyl groups of 2,2-dimethyloxazolidines, the diastereotopicity of the

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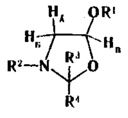
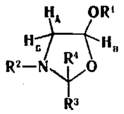
TABLE 1. PMR Spectra of Oxazolidines



trans



cis

IX, X, XIII–XV R^2=Ts; XI R^2= $p\text{-}O_2NC_6H_4SO_2$; IX, XI–XV R^1=CH_3; X R^1=C_2H_5

Compound	R^3	R^4	Percentage of the cis isomer,	Isomer	Chemical shifts, δ, ppm					Spin–spin coupling constants, Hz			Solvent
					HA	HB	HC	R^1= =CH_3	R^3, R^4 (J, Hz)	cis	trans	gem	
IX	CH_3	CH_3	—	—	3,47	3,58	4,98	3,28	1,56s, 1,61s	4,3	1,5	9,8	$CHCl_3$
X	CH_3	CH_3	—	—	3,50	3,58	5,09	R^1= =C_2H_5*	1,56s, 1,61s	4,3	2,3	9,5	$CHCl_3$
XI	CH_3	CH_3	—	—	3,60	3,69	5,05	3,30	1,610 s, 1,626 s	4,3	1,7	9,5	CCl_4
XII	iso-C_4H_9	iso-C_4H_9	—	—	3,21	3,55	4,89	3,30	0,83—0,94m[12H], 1,5—1,9m[4H]	5,1	1,9	9,5	CCl_4
XIII	CH_3	C_2H_5	22	trans	3,29	3,55	4,92	3,27	1,46s [3H], 0,92t, 1,91dq and 1,98dq [5H] (J_{gem} = 10 Hz, J_{vic} = 7 Hz)	5,2	2,0	9,8	CCl_4
				cis	3,40	3,51	4,93	3,24	1,52s [3H], 0,85t, 1,84dq, 1,91dq [5H] (J_{gem} = 10 Hz, J_{vic} = 7 Hz)	4,3	2,0	10	
XIV	CH_3	C_6H_5	7	trans	3,39	3,96	5,09	3,22	1,93s, 7,20m	5,7	3,4	10,8	$CHCl_3$
				cis	3,7	3,7	5,1	3,11	2,01s				
XV	CH_3	$C_6H_5CH_2$	†	trans	3,10	3,54	4,94	3,23	1,35s[3H], 3,1—3,3m[2H], 7,2m[5H]	5,1	2,0	9,5	CCl_4

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*1.11 t, 3.40 dq, 3.69 dq (5H, J_{gem} = 9.6 Hz, J_{vic} = 7.2 Hz).

†The percentage of the cis isomer does not exceed 10%.

TABLE 2. Characteristics of the Oxazolidines

Compound	mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %*
			C	H	N	S	C	H	N	S	
IX	58,2— 58,6	$C_{13}H_{19}NO_4S$	54,9 54,8	6,9 7,0	5,2 5,3	10,9 10,7	54,7	6,7	4,9	11,2	40
X	79,4	$C_{14}H_{21}NO_4S$	55,9 56,3	6,7 6,8	4,8 4,8	10,5 10,8	56,2	7,1	4,7	10,7	39
XI	120,5—121	$C_{12}H_{16}N_2O_6S$	45,2 45,2	5,1 5,0	8,7 8,6	10,0 10,0	45,6	5,1	8,9	10,1	19
XII	Oil†										7
XIII	Oil	$C_{14}H_{21}NO_4S$	56,2 55,9	7,2 7,0	4,2 4,3	10,8 11,0	56,2	7,1	4,7	10,7	26
XIV	110,5—110,7	$C_{18}H_{21}NO_4S$	63,0 62,8	6,1 6,1	3,6 3,5		62,2	6,1	4,0		14
XV	Oil†										13

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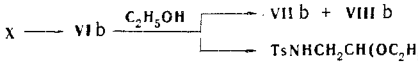
* The overall yield of piperazine VII and polymer VIII was 50% (in the synthesis of oxazolidine IX), 47% (in the synthesis of oxazolidine X), and 65% (in the synthesis of oxazolidine XI).

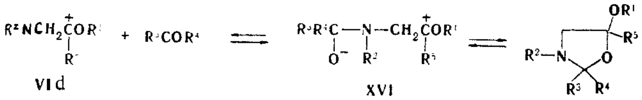
† We were unable to isolate analytically pure samples of the oxazolidines.

methylene groups of the ethoxy group in 5-ethoxyoxazolidine X, and the presence of an ABX system of ring protons [the signals of the latter are split by long-range spin–spin coupling into a quartet in the case of 5-methoxyoxazolidines and into a triplet in the case of 5-ethoxyoxazolidine (J = 0.4 Hz)].

N-Tosylaminoacetaldehyde diethylacetal and acetone (in 30 and 70% yields, respectively), as well as piperazine VIIb and polymer VIIIb, are formed when an alcohol solution of oxazolidine X is heated at 150°. A similar conversion of oxazolidine X to a mixture of VIIb and VIIIb may also occur when an inadequately dried sample of X is allowed to stand.



Thus under certain conditions one may expect the establishment of an equilibrium between the 5-alkoxyoxazolidine and the mixture of carbonyl compounds and dipolar ions VI. Since the reversible formation of oxazolidines from the VIb ion competes with the irreversible polymerization of the latter, the yield of oxazolidine X decreases when the experimental time is increased (40% at 40° for 2 h, 13% at 40° for 15 h). It is most likely that the first step in the formation of the oxazolidines is reversible nucleophilic addition of ion VI to the carbonyl compound to give ion XVI (R = H). This is in agreement with the data in [3], with the absence of products of cycloaddition of ion VI to the C = C bond of vinyl ethers I and II, and with the dependence of the yields of the oxazolidines on the nature of the substituents in the ketones (Table 2). Thus dimer VII and polymer VIIIa are formed in the reaction of ester I, azide III, and 3,3-dimethyl-2-butanone; according to the PMR spectral data, the reaction mixture does not contain compounds with an oxazolidine ring.



The rate of cyclization of ion XVI (R^5 = H) to oxazolidines is evidently comparable to the rate of the reverse reaction of conversion to ion VId (R^5 = H), since the yields of oxazolidines do not exceed 40%. The fact [1] that 2-methyl- and 2-phenyl-2-alkoxyaziridines are not converted to oxazolidines in the presence of acetone and acetaldehyde can be explained by the decrease in the electrophilicity of ion XVI ($R^5 = CH_3$, C_6H_5).

5-Methoxy-2,2-diisobutyl-3-tosyloxazolidine (XII) was isolated in low yield (7%) in the reaction of tosylazide with ether I in the presence of 2,6-dimethyl-4-heptanone, whereas oxazolidines XIII-XV were obtained in low yields in the reaction with unsymmetrical ketones. In this case both the cis- and trans-isomeric oxazolidines are usually formed (the large grouping attached to C_2 with respect to the alkoxy group attached to C_5 of the oxazolidine ring). It follows from the PMR spectrum that oxazolidine XIII is a mixture of cis and trans isomers in a ratio of 1 : 3.5. The assignment of the configuration was made in analogy with the data for trans-5-methoxy-2-methyl-3-tosyloxazolidine (XVII) [5]. It is apparent from Table 1 that the characteristics of the ring system of ABX protons of oxazolidine XIII, which is present in smaller amounts, are similar to the same characteristics of oxazolidines IX-XI, and the PMR spectrum of the principal isomer is analogous to the spectrum of oxazolidine XVII.

The high percentage of trans-oxazolidine XIII in the mixture of isomers (78 ± 3%) indicates the high stereoselectivity of the cyclization of the corresponding dipolar ion XVI; this is associated with the low reactivity of this ion. The percentage of the cis isomers in oxazolidines XIV and XV is small (determined from the ratio of the areas of the signals of the CH_3O and CH_3 groups in the PMR spectra; see Table 1). The IR spectra of XIII-XV are similar to the IR spectra of oxazolidines IX-XI.

The reaction mixture of ether I, azide III, and 2,4-pentanedione was analyzed, after separation by preparative TLC, by means of IR and PMR spectroscopy. Only diazo-transfer products – tosylamide and 3-diazo-2,4-pentanedione – were isolated from the complex mixtures and identified. We were also unable to obtain the corresponding oxazolidine in the reaction of ether I, azide III, and 2,3-butanedione.

EXPERIMENTAL

The PMR spectra were recorded with a Varian-HA-100 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of CCl_4 solutions of liquid oxazolidines XII and XIII and of mineral oil suspensions of the solid oxazolidines were obtained with a UR-20 spectrometer. The characteristic frequencies for the oxazolidines were observed in the following intervals: 1350-1360, 1165-1170 (SO_2 asym- and sym-stretching vibrations), 670-690, 655-670, 600-625 (SO_2 scissors deformation vibrations), 555-585 (fan vibrations), and 540-560 cm^{-1}; the assignment of the frequencies in the IR spectrum was made from the data in [6].

Activity II aluminum oxide or Silufol UV-254 was used for analytical TLC, whereas LS_{254} 5/40 silica gel with a luminescent indicator was used for preparative TLC; elution in all cases was accomplished with hexane–acetone (3 : 1). Column chromatography was carried out with the same aluminum oxide and elution with hexane–acetone (varying concentrations).

The alkyl vinyl ethers were purified by distillation over sodium, and tosyl azide (mp 21°) was purified by column chromatography. p-Nitrobenzenesulfonyl azide (IV) was obtained in 68% yield from p-nitrobenzenesulfonyl chloride and hydrazine hydrate [7] and had mp 100-102°. The commercial-grade ketones were dried thoroughly and distilled with a column (five theoretical plates).

Reaction of Tosyl Azide with Ethyl Vinyl Ether in Acetone. A mixture of 22 g of the azide, 20 ml of the ether, and 20 ml of acetone was allowed to stand overnight after the initial strongly exothermic reaction ceased. The precipitate was removed by filtration, washed with acetone, and dried to give 0.6 g (2%) of 2,5-diethoxy-1,4-ditosylpiperazine (VIIb) with mp 170° (dec.) (see [4]). The IR and PMR spectra were identical to the spectra of the piperazine obtained in [4]. The filtrate was diluted with hot hexane, and the polymer was separated. The filtrate was frozen out to yield 13 g (39%) of crude 5-ethoxy-2,2-dimethyl-3-toxyloxazolidine (X). An analytically pure sample (mp 79.4°) was obtained by preparative chromatography on aluminum oxide and subsequent recrystallization from hexane. IR spectrum: 1348, 1168, 685, 650, 610, 578, 550 cm^{-1}. Evaporation of the filtrate yielded 12 g (45%) of polymer VIIIb. When the crude oxazolidine was allowed to stand for 24 h, it was converted to a mixture of piperazine VIIb and polymer VIIIb.

5-Methoxy-2,2-dimethyl-3-(p-nitrophenylsulfonyl)oxazolidine (XI). A mixture of 4.56 g (2.0 mmole) of azide IV, 3.48 g (6.0 mmole) of ether I, and 3.48 g (6.0 mmole) of acetone was heated in a sealed tube at 40° for 2 h, after which it was treated repeatedly with hot hexane. Evaporation of the hexane extract yielded 1.18 g (19%) of oxazolidine XI with mp 120.5-121° [from hexane–chloroform (9 : 1)]. IR spectrum: 1348, 1168, 682, 610, 583, 561 cm^{-1}. The hexane-insoluble residue from the reaction mixture (4.7 g) was, according to the PMR spectral data, a mixture of starting azide IV, oxazolidine XI, and polymer VIIIc.

5-Methoxy-2,2-dimethyl-3-tosyloxazolidine (IX). This compound was similarly obtained. In the synthesis of oxazolidines XII-XV the molar ratio of azide III, ether I, and carbonyl compounds was 1 : 3 : 3, and the reactions were carried out in sealed tubes at 40° for 2 h; oxazolidines XII-XV (Table 2) were isolated by preparative TLC on silica gel, since they were formed in low yields as poorly crystallizable mixtures of isomers. In the isolation of the oxazolidines by means of TLC we were able to determine the conversion of the azide but were unable to determine the amount of polyaziridine VIIIa formed. In the isolation of oxazolidines XII-XV the yields of the reaction products and the recording of the PMR spectra were accomplished after separation of the reaction by means of TLC; analytically pure samples were used for recording of the IR spectra.

Thermolysis of 5-Ethoxy-2,2-dimethyl-3-tosyloxazolidine in Ethanol. A solution of 1.8 g of the oxazolidine in 50 ml of anhydrous ethanol was heated in a sealed tube at 150° for 3 h, after which the alcohol was removed by distillation, and the residue was treated with hot hexane to give 0.5 g (30%) of N-tosylaminoacetaldehyde diethylacetal with mp 66-67°; this product was identified by comparison with an authentic sample [4] from the IR spectra and the results of TLC on aluminum oxide. The hexane-insoluble residue was found to be polymer VIIIb (30%). A 1.2-g sample of 2,4-dinitrophenylhydrazine in 60 ml of 20% hydrochloric acid was added to the alcohol solution, and the resulting precipitate was removed by filtration and washed with water and alcohol to give 1.05 g (70%) of acetone 2,4-dinitrophenylhydrazone. No melting-point depression was observed for a mixture of this product with an authentic sample.

Reaction of Tosyl Azide with Methyl Vinyl Ether in 2,4-Pentanedione. A mixture of 1.96 g of the azide, 1.1 ml of ether I, and 1.5 ml of 2,4-pentanedione was heated at 40° for 2 h, after which it was subjected to preparative separation on silica gel with elution by CCl_4-CHCl_3 (1:1) to give the tosylamide, with mp 137° (successively from water and toluene) and R_f 0.1, in 25% yield. PMR spectrum, δ (nitrobenzene): 2.26 (s, 3H) and 5.7 ppm (s, 2H). The PMR spectra of the fractions with R_f 0.2 and 0.4 did not contain signals of the ring system of the protons of oxazolidine and singlet signals of methyl groups of 2,4-pentanedione. The more mobile fractions contained tosyl azide (15%), which was identified from its IR spectrum, and 3-diazo-2,4-pentanedione (18%). PMR spectrum, δ (CCl_4): 2.29 ppm (s). IR spectrum (CCl_4): 1690 (C=O) and 2110 cm^{-1} (diazo group). An authentic sample of the diazo ketone obtained by the method in [8] had spectra analogous to those of the product.

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ISOMERIC DISTYRYLBENZOBISOXAZOLES

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Isomeric 2,6-distyrylbenzobisoxazoles, the UV spectra of which provide evidence of a difference in the conjugation of the styrylbenzoxazole fragments in their molecules, were synthesized by condensation of isomeric 2,6-dimethylbenzobisoxazoles with aromatic aldehydes.

The heteroanalogs of stilbene and distyrylbenzene, which contain benzoxazole structural fragments, are of considerable interest both for the study of the relationship between the structure of organic compounds and their spectral-luminescence properties and from the point of view of their application as, for example, optical bleaches [1], luminophores, and generating compounds for quantum electronics [2].

In the present communication we describe the preparation of isomeric 2,6-distyrylbenzo[1,2-d;5,4-d']- (I) and 2,6-distyrylbenzo[1,2-d; 4,5-d']bisoxazoles (II), which are heteroanalogs of distyrylbenzenes. The condensation of 2-methylbenzoxazole with aromatic aldehydes (for example, fusion with zinc chloride [3] or boric acid [4] or refluxing in methanol in the presence of alkaline agents [5]), which gives the products, in low yields, is usually employed for the synthesis of styryl-substituted benzoxazoles.

We have developed a method for the synthesis of distyrylbenzobisoxazoles I and II by condensation of 2,6-dimethylbenzo[1,2-d; 5,4-d']- (III) and 2,6-dimethylbenzo[1,2-d; 4,5-d']bisoxazole (IV), respectively, with aro-

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