

REACTION OF ALKENE OXIDES WITH AROMATIC THIONYLIMINES

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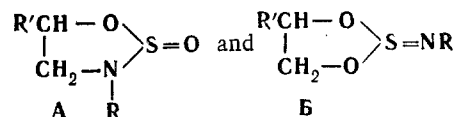
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The oxides of ethylene and propene, and epichlorohydrin, react with thionylanilines ($\text{ArN}=\text{S}=\text{O}$) in the presence of tetraethylammonium bromide catalyst at $95^\circ\text{--}100^\circ\text{C}$ to give N-arylalkeneamidosulfites, whose structures are confirmed by retrosynthesis from the corresponding N-phenylamino alcohols, and thionyl chloride, as well as by their IR spectra.

It is known that isocyanates ($\text{RN}=\text{C}=\text{O}$) react with alkene oxides to give oxazolid-2-ones [1, 2]. Isothiocyanates ($\text{RN}=\text{C}=\text{S}$) react either to give spiran compounds (1, 3, 5-trimethylhexahydrotriazine-2, 6-dithione-4-spiro-2'-thioxalanes-1, 3') [3, 4], or via intermediate formation of iminothiooxalanes, also give oxazolid-2-ones [5]. There the isocyanate and isothiocyanate molecules react at the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ bonds, the $\text{N}=\text{C}$ bond being unaffected.

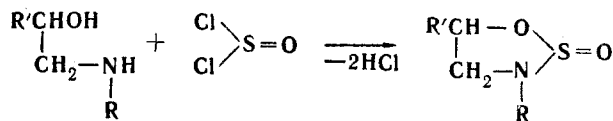
Up to the present the reaction of alkene oxides with formal analogs of isothiocyanates, viz., the so-called thionylimines $\text{RN}=\text{S}=\text{O}$, had not been studied. It was of interest to study the reaction between such oxides and aromatic thionylamines, in order to prepare heterocyclic compounds, and to determine the relative reactivities of the $\text{N}=\text{S}$ and $\text{S}=\text{O}$ bonds towards the oxides. Reactions of alkene oxides with the $\text{S}=\text{O}$ bond have previously been investigated for sulfur dioxide [6].

The structure of the thionylimine molecule would lead one to expect formation of two different types of reaction products:

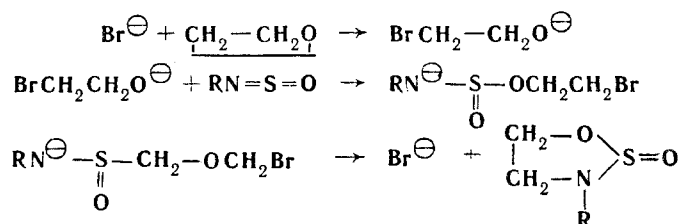


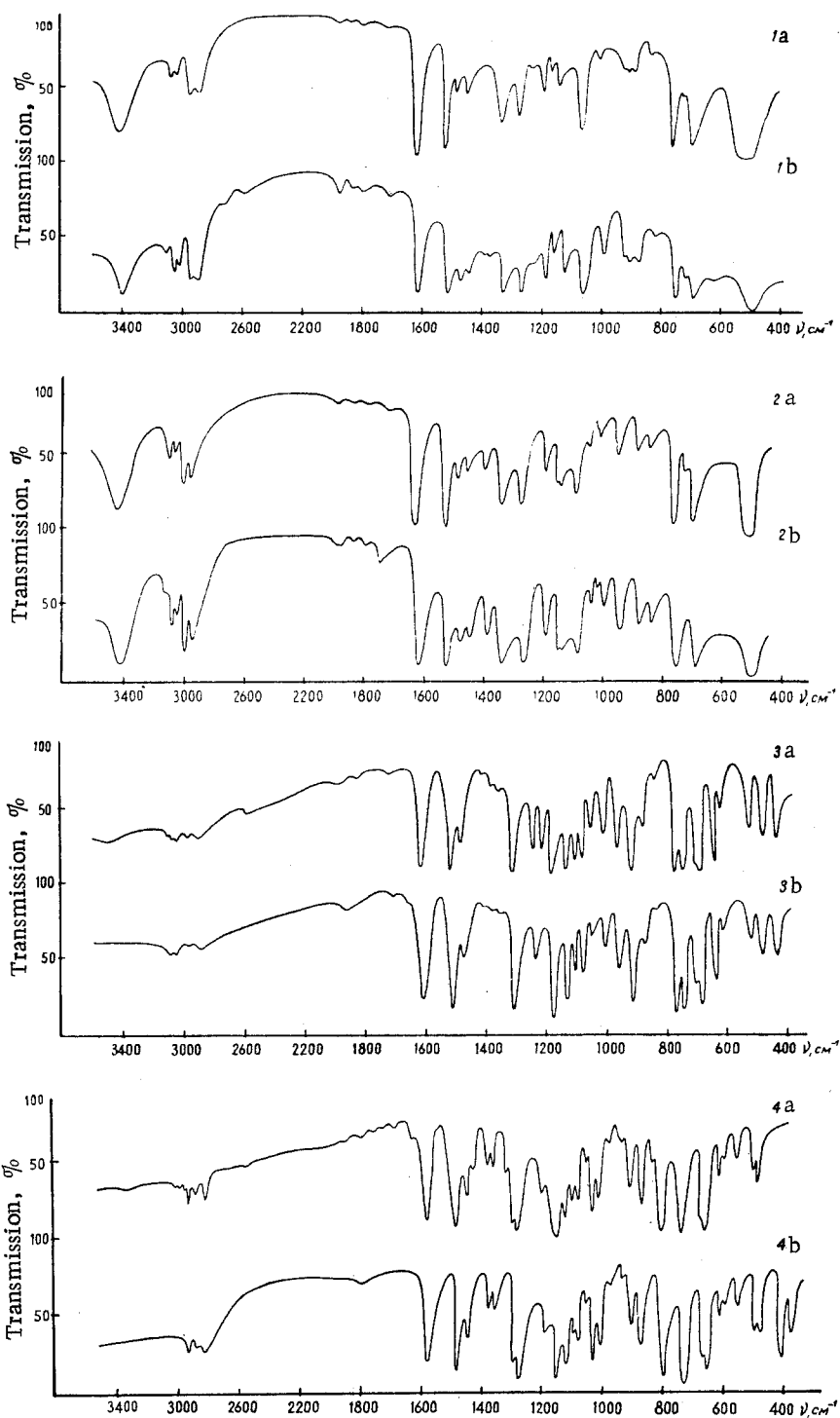
Our work showed that reaction of thionylanilines with ethylene and propene oxides, and with epichlorohydrin, in the presence of tetraethylammonium bromide catalyst proceeds with formation of structure A compounds.

These compounds are readily hydrolyzed by 10% hydrochloric acid, with evolution of sulfur dioxide, to give the corresponding N-phenylamino alcohols, with IR spectra identical with the amino alcohols obtained by reacting the alkene oxides with aniline (figure, plots 1a, 1b, 2a, 2b). In addition, the compounds obtained were retrosynthesized. Thus N-(2-hydroxyethyl)aniline and N-(2-hydroxypropyl)aniline react with thionyl chloride to give I and II (see table), from their IR spectra (plots 3, 4) identical with the compounds obtained from thionylaniline:



It may be assumed that the mechanism of the reaction between alkene oxides and the thionylaniline in the presence of tetraethylammonium bromide is





IR spectra. 1) N-(2-Hydroxyethyl)aniline: a) obtained by hydrolysis; b) ex aniline and ethylene oxide; 2) N-(2-hydroxypropyl)aniline: a) obtained by hydrolysis; b) ex aniline and propene oxide; 3) N-phenylethylenamidosulfite: a) ex ethylene oxide and phenylthionylimine; b) ex N-(2-hydroxyethyl)aniline and thionyl chloride; 4) N-phenylpropenamidosulfite: a) ex propene oxide and phenylthionylimine; b) ex N-(2-hydroxypropyl)aniline and thionyl chloride.



Com- pound num- ber	Epoxide used	Reac- tion time, hr	Product			Mp, °C	Character- istic bands		Formula	Found						Calculated				Yield*
			R	R'	R''		ν_1, cm^{-1}	ν_2, cm^{-1}		C, %	H, %	N, %	S, %	M	C, %	H, %	N, %	S, %	M	
I	Ethylene oxide	12	C ₆ H ₅	H	H	47	1178	1309	C ₈ H ₉ N ₂ S	52.14 52.55	5.00 5.03	7.13 7.22	17.39 17.07	180.3 181	4.92	7.65	17.48	183	36	
II	Ethylene oxide	6	<i>p</i> -CH ₃ C ₆ H ₄	H	H	76	1176	1292	C ₉ H ₁₁ NO ₂ S	54.79 54.48	5.67 5.37	6.85 6.83	15.76 15.80	192.5 193	5.58	7.11	16.24	197	20	
III	Ethylene oxide	6	<i>p</i> -ClC ₆ H ₄	H	H	73	1180	1312	C ₈ H ₆ ClNO ₂ S**	44.52 44.46	3.76 3.74	6.25 6.30	14.30 14.30	214 215	3.68	6.43	14.71	217.5	28	
IV	Ethylene oxide	1	<i>p</i> -NO ₂ C ₆ H ₄	H	H	143	1190	1321	C ₈ H ₆ N ₂ O ₄ S	42.10 42.01	3.55 3.51	12.16 12.18	13.94 13.92	230 233	3.50	12.28	14.03	228	90	
V	Propylene oxide	20	C ₆ H ₅	H	CH ₃	57	1178	1309	C ₉ H ₁₁ NO ₂ S	54.29 54.49	5.76 5.46	6.72 6.82	16.31 16.24	191 194	5.58	7.11	16.24	197	45	
VI	Epichloro- hydrin	2	C ₆ H ₅	CH ₂ Cl	H	95	1160	1282	C ₉ H ₁₀ ClNO ₂ S***	46.85 46.31	4.25 4.41	5.93 6.23	13.75 13.50	230 227	4.32	6.04	13.82	231.5	11 41	
VII	Epichloro- hydrin	2	C ₆ H ₅	H	CH ₂ Cl	55	1166	1310	C ₉ H ₁₀ ClNO ₂ S****	46.64 46.62	4.22 4.42	5.88 5.89	14.12 13.51	230.5 228	4.32	6.04	13.82	231.5	30	
VIII	Ethylene oxide	6	α -C ₁₀ H ₇	H	H	61	1170	1285	C ₁₂ H ₁₁ NO ₂ S	61.89 61.65	4.82 4.75	6.10 6.23	13.95 13.97	237 231	4.71	6.00	13.73	233	51	

* Calculated on the thionylimine.

** Found: Cl 16.20, 16.20%. Calculated: Cl 16.32%.

*** Found: Cl 15.39, 15.42%. Calculated: Cl 15.33%.

**** Found: Cl 15.20, 15.45%. Calculated: Cl 15.33%.

The bromine anion opens the oxide ring to give an anion, which attacks the N=S link of the thionylaniline, to give a nitrogen anion. The latter splits off a bromine anion, and undergoes ring closure. If this mechanism is correct, lowering the electron density at the sulfur atom should facilitate the reaction. The N=S=O group is known to be conjugated with the aromatic ring [7], consequently introduction of electron-accepting substituents at the ortho and para positions in the benzene ring should give rise to considerable decrease in electron density at the sulfur atom as compared with electron-donating substituents, leading to more favorable conditions for the reaction to proceed. Actually it was found that p-nitrophenylenethionylimine reacts more readily with ethylene oxide than phenylthionylimine, p-tolylene-thionylimine, or p-chlorophenylenethionylimine. Even at room temperature a high yield is obtained in less time (table).

The IR spectra of all the compounds prepared were determined. The $\text{N}=\text{S}=\text{O}$ group is characterized by two absorption bands in the $1100\text{--}1330\text{ cm}^{-1}$ range: $\nu_1 \sim 1160\text{--}1190$ and $\nu_2 \sim 1280\text{--}1321\text{ cm}^{-1}$.

The position of the ν_1 band depends on the kind of substituent in the benzene ring. Electron-accepting substituents at the para position displace it in the longer wave numbers direction, and electron-donating ones towards shorter wave numbers (table). This is in agreement with data relating to the IR spectra of thionylanilines [8].

Reaction of phenylthionylimine with epichlorohydrin led to the isolation of two isomers, differing with respect to the position of the nitrogen atom opposite the chloromethyl group. They owed their formation to different directions of opening of the epoxide ring. Reviewing the spectra of compounds V, VI, and VII, it can be assumed that VI has the chloromethyl group nearest the N-S bond, since the ν_2 is markedly displaced with respect to that of V, while the ν_2 bands of V and VII are practically identical.

Experimental

The thionylanilines and thionyl- α -naphthylamine were prepared as has been described [9], by reacting the appropriate amines and thionyl chloride in benzene solution at $95^\circ\text{--}100^\circ\text{C}$.

Reacting thionylanilines with alkene oxides. The appropriate thionylaniline and alkene oxide, mole ratio 1 : 2, plus 1% tetraethylammonium bromide based on the oxide, were sealed together in a tube, and heated at $95^\circ\text{--}100^\circ\text{C}$. Crystals were obtained on cooling an ether solution of the reaction products; they were recrystallized from ether, using active charcoal. White crystalline compounds were obtained. The rest comprised unreacted thionylamine and resins. With p-nitrophenylenethionylamine, a 3-fold excess ethylene oxide was used, and 40 hr reaction at 20° gave an almost quantitative yield of pale-yellow crystals (ex acetone).

In the case of the reaction of epichlorohydrin with phenylthionylimine, the isomers were separated by fractional crystallization from benzene. The table gives the reaction time, melting point, characteristic absorption bands, and analytical data for the amidosulfinic acid cyclic esters.

Retrosyntheses of N-phenylethylene (propylene)amidosulfites. A solution of 0.1 mole N-(2-hydroxyethyl)aniline and 0.25 mole Et_3N in 50 ml was cooled to -70° and stirred, then the thionyl chloride (0.1 mole) in 50 ml ether added over 30 min, after which the products were kept below 0°C for 2 hr. The precipitate was filtered off and washed with ether. The ether was dried over Na_2SO_4 , and then gave white crystals of I, yield 10–15%, mp 45° (ex ether). Undepressed mixed mp with the product from phenylthionylimine and ethylene oxide. Compound V was prepared similarly.

Hydrolysis of N-arylalkenamidosulfites I and V. 3 g I (or V) was placed in 35 ml 10% HCl. It quickly dissolved with evolution of SO_2 , and the mixture was held at $95^\circ\text{--}100^\circ\text{C}$ for 30 min. Then the solution was neutralized with K_2CO_3 and extracted with ether. The extracts were dried over Na_2SO_4 , and vacuum-fractionated, to give a cut bp 112° (2 mm), yield of N-(2-hydroxyethyl)aniline 1.8 g. A cut bp 122° (3 mm), mass 1.9 g, was N-(2-hydroxypropyl)aniline.

IR spectra were measured with a double-beam UR-10 spectrophotometer in the $400\text{--}3600\text{ cm}^{-1}$ region. Samples of the solids were tabletted with KBr (compound concentration with 1%), while liquids were observed as thin films between KBr crystals.

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