SYNTHESIS OF SULFUR-CONTAINING SUBSTANCES FROM VINYL ETHERS AND ACETYLENE COMMUNICATION 23. OXIDATION OF VINYL SULFIDES AND SOME PROPERTIES OF VINYL SULFOXIDES AND SULFONES

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The oxidation of organic sulfides is at present attracting much attention from investigators, particularly in connection with the study of the nature of the autoxidative processes occurring in the aging of vulcanized rubber [1, 2]. It was shown that, both in autoxidation and in oxidation with alkyl hydroperoxides, very often not only simple oxidation products (sulfoxides) are formed [1], but also complex decomposition products [2]. The latter include, in particular, unsaturated sulfides of the allyl type and cyclic sulfides with a vinyl double bond [2].

We were interested in the optimum conditions for the oxidation of vinyl sulfides to vinyl sulfoxides and sulfones, i.e., oxidation with preservation of the double bond. Kohler and Potter [3] showed that oxidation of the stereoisomeric styryl tolyl sulfides with hydrogen peroxide in glacial acetic acid at low temperature gives an almost quantitative yield of a mixture of stereoisomeric sulfoxides or sulfones. Kochetkov and Vinogradova [4] have recently used similar conditions for the oxidation of the 2-acylvinyl aryl sulfides (RCOCH=CHSAr) which they synthesized. The yields of sulfoxides were 25-60%, and the yields of sulfones were 30-40% for R = alkyl and 96% for R = aryl.

However, for unsubstituted vinyl sulfides of the aliphatic series the optimum conditions of oxidation have apparently not been found. Thus, Price and Gillis [5] obtained 17% of methyl vinyl sulfoxide by the oxidation of methyl vinyl sulfide with sodium hypochlorite; from the same sulfide the sulfone was obtained in only 16%yield by oxidation with hydrogen peroxide in glacial acetic acid [5]. Hence, further investigations have not confirmed earlier claims in a German patent [6] for a method of preparation of vinyl sulfoxides and sulfones in good yield from various vinyl sulfides by the action of such oxidizing agents as hydrogen peroxide, sodium hypochlorite, etc. The object of the present work was the determination of the conditions for the selective oxidation of sulfur in vinyl sulfides, mainly of the aliphatic series, and the study of some properties of vinyl sulfoxides and sulfones.

We showed that, for the preparation of vinyl sulfoxides in good yield (60-70%) and as the only reaction product, it is best to carry out the oxidation in an acetone^{**} medium with an equimolecular amount of 70-80% hydrogen peroxide:

$$CH_2 \approx CHSR \xrightarrow[-5+20^\circ; 43-50]{H_2O_3} CH_2 = CHSOR$$

^{*} Deceased

^{**} In methanol the yield of sulfoxide is somewhat lower.

TABLE 1

Vinyl Sulfoxides $CH_2 = CHSOR$

R	B.p. in °C (p in mm)	n_D^{20}	[<i>d</i> ²⁰ ₄	Unoxidized sulfide (%)	Yield(% on sulfide taken)	
					sulfoxide	sulfone
CH3* C2H5 C3H7 C4H7 C4H9 C4H9OCH2CH2 C4H9OCH2CH2 C6H5**	58,5-59°(6) 54,5(2) 83(8) 8083(2) 113114(2) 104106(2)	1,4951 1,4900 1,4870 1,4830 1,4765 1,5869	1,0876 1,0422 1,0125 0,9891 1,0138 1,1629	not determined 10-2 8 20 20	70 60-75 60-70 65-75 44-58 58-74	 4-5

* The literature [5] gives b.p. 46-47° (0.8 mm).

** The literature [8] gives b.p. 93-95° (0.2 mm). The other vinyl sulfoxides are not described in the literature.

Despite the long duration of the experiment, part of the sulfide remains unoxidized. This indicates that the sulfur atom in vinyl sulfides is substantially less reactive than that in saturated sulfides [7] evidently because of reduction in the accessibility of the electrons of sulfur due to conjugation of the type

$$CH_2 = CH - SR$$

If 27-30% peroxide is used in the oxidation, as earlier recommended in the patent [6], the yield of sulfoxide does not exceed 50-55%. Oxidation with 30% peroxide in formic acid leads to a complex mixture of oxidation and addition products.

The lower alkyl vinyl sulfoxides are mobile liquids, readily soluble in water and most organic solvents, distillable in a vacuum without decomposition*, and stable to keeping in a sealed tube for a long time without darkening. The properties of the vinyl sulfoxides are given in Table 1.

For the preparation of vinyl sulfones it was earlier recommended [6] that vinyl sulfides be heated with excess of 30% hydrogen peroxide in presence of pyridine. We showed that only aryl vinyl sulfones could be prepared in this way in good yield. In the oxidation of alkyl vinyl sulfides, rise in reaction temperature leads to the formation of a mixture of vinyl sulfoxides, vinyl sulfones, and particularly water-soluble substances of a polymeric character.

Vinyl sulfones may be obtained by the oxidation of vinyl sulfides with peroxybenzoic acid (Prilezhaev's reagent **) or peroxyacetic acid (Table 2):

 $CH_2 = CHSR \xrightarrow{2C_4 \Pi_5 COOOH} CH_2 = CHSOR \longrightarrow CH_2 = CHSO_2 R.$

* Alkyl vinyl sulfoxides do not stand overheating and were therefore fractionated from a small flask with a short column. When an attempt was made at fractionation at 5-7 mm through an all-glass column (height of working part 40 cm), ethyl vinyl and, particularly, butyl vinyl sulfoxides partly decomposed.

** Lewin [9] used this reagent for the oxidation of divinyl sulfide to the sulfoxide and sulfone and also for the quantitative titration of sulfide sulfur.

TABLE 2

Vinyl Sulfones $CH_2 = CHSO_2R$

	B.p. in °C (p in mm)	n ²⁰ _D	d ₄ ²⁰	Yield in different methods			
R				30% H ₂ O ₂	$\mathrm{H_2O_2+} +\mathrm{SeO_2}$	Peroxy acid	
C_2H_5*	8788(2)	1,4643	1,1497	21,2	71	75 (CH ₃ OOOH) 66 (C₀H₅COOOH)	
C ₃ H ₇	98100(3)	1,4642	1,1060		66	,	
C ₄ H ₉ **	116-117(5)	1,4630	1,0776	39,7	55-60		
C ₆ H ₅ ***	m.p. 67,5—68		ana a start	55 ,3		No. 1997	

* The literature gives: b.p. 107° (9 mm); n²¹_D 1.4622 [12]; b.p. 106-108° (8 mm) [13]; b.p. 84-85° (1 mm) [14].

** The literature [15] gives b.p. 135° (15 mm).

*** The literature gives: m.p. 68.5° [16]; m.p. 72° [12]; m.p. 67.5-68.5° [17].

TABLE 3

Molecular Refractions of Vinyl Sulfides, Sulfoxides, and Sulfones*

	CH ₂ =CHSR MR		CH2=CHSOR		CH2CHSO2R MR	
R	found	calcu- lated	found	calcu- lated	found	calcu- lated
CH3 C2H5 C3H7 C4H9	28,37 32,89 37,47	28,04 32,78 37,40	24,16 28,88 33,52 38,17	24,059 28,67 33,41 38,03	28,88 33,44 37,83	28,64 33,38 37,99
C ₄ H _p OCH ₂ CH ₂ C ₆ H ₅	48,50 44,05	48,28 43,60	49,06 43,44	48,91 43,67		

* In the calculation the following values of atom and group refractions were used: S in dialkyl sulfides 7.96 and in alkyl aryl sulfides 8.52 [25]; >SO 8.59 and >SO₂ 8.56 [26].

The double bond remains intact, which is indicated by the absence of residues of polymer. The vinyl sulfones obtained in this way contain small amounts of unoxidized sulfoxides as impurity, and it is difficult to purify them from these. Hence, for preparative purpose it is much more convenient to oxidize the sulfide to sulfone with excess of concentrated hydrogen peroxide in t-butyl alcohol in presence of selenium dioxide (at least 5 g per mole of H_2O_2). By this method we were able to prepare vinyl sulfones not containing sulfoxides as impurity (Fig. 1). In this case the oxidizing agent appears to be selenic acid, as earlier suggested by Smith and Holm [10], who proposed oxidation with hydrogen peroxide in presence of SeO₂ as a method for the preparation of acrylic and methacrylic acids from the corresponding aldehydes. Under comparable conditions, hydrogen peroxide in t-butyl alcohol, but without SeO₂, and also t-butyl hydroperoxide oxidize vinyl sulfides only to sulfoxides. No side reactions were observed in oxidation in presence of SeO₂, though for other unsaturated compounds this compound is a fairly good catalyst for the hydroxylation of double bonds with H_2O_2 [11].

In recent literature [5, 17-23] there has been a renewal of interest in the question of the nature of the S-O bond in sulfoxides and sulfones, is it a true double bond with participation of the <u>d</u> shell of sulfur or a singly covalent semipolar bond with preservation of the octet around the sulfur atom? From our point of view



Fig. 1. Ultraviolet absorption spectra of vinyl sulfones: 1) ethyl vinyl sulfone prepared by oxidation with BzOOOH; 2) ethyl vinyl sulfone prepared by oxidation with H_2O_2 + +SeO₂; 3) proply vinyl sulfone prepared likewise; 4) butyl vinyl sulfone prepared likewise.

the posing of the question in such a categorical form is not altogether correct, because in the real molecule the bond probably has an intermediate character with partial participation of the <u>d</u> shell. In any case, proofs that the bond has this or the other nature, as given in previous papers, are not very convincing. Thus, as one of the proofs of the semipolar nature of this bond is given the fact that the molecular refraction rises by a very small amount as we pass from sulfides to the corresponding sulfoxides and sulfones [5, 25]. The same regularity is observed in the series of compounds that we synthesized (Table 3). However, this can be explained with equal success by the properties of S = O bonds formed with participation of the <u>d</u> electrons of the S atom.

Moreover, Price and co-workers consider [5, 17, 22, 23] that the character of the ultraviolet and infrared spectra of some vinyl sulfones and sulfoxides also favors the view that the S-O bond is semipolar because these authors did not detect any clear signs of the conjugation of C = C and S = O groupings in these spectra. For the substances synthesized we determined the ultraviolet absorption spectra and also the intensities of some characteristic lines in the Raman spectra (Table 4).

These results show that there are indications in the spectra that conjugation exists in vinyl sulfoxide and sulfone molecules. Thus, the C = C

frequencies in the Raman spectra are appreciably lower than those of olefins, though there is no appreciable increase in intensity. For S-O bonds there is no lowering of frequency as compared with the saturated sulfoxide or sulfone, but the intensity is greatly different, being lower in the unsaturated compounds. Hence, there is undoubtedly some interaction of S-O groups with double bonds, but these data are inadequate for the purpose of determining the nature of the S-O bond. As regards the ultraviolet spectra, we found that in heptane all the vinyl sulfoxides have a fairly intense maximum at 247 m μ which is substantially displaced from the maximum of saturated sulfoxides and permits the detection of even small amounts of vinyl sulfoxide impurity in vinyl sulfones. This will be seen from Fig. 1, in which Curve 1 refers to a sample of ethyl vinyl sulfide containing 1-2% of sulfoxide impurity and obtained by the oxidation of the sulfide with peroxybenzoic acid. Vinyl sulfones prepared by oxidation in presence of SeO₂ (Curves 2-4) did not contain such impurities. When the ultraviolet spectra of vinyl sulfoxides were determined in alcohol, there was a considerably less intense maximum at about 230 m μ , probably because of interaction with the solvent (Fig. 2). This led Price and Gilbert [22] into error: they used the ultraviolet spectrum of methyl vinyl sulfide as evidence of weak conjugation in this molecule and therefore of the purely semipolar nature of the S-O bond, which probably does not correspond with reality.

In conclusion we may point out that in this paper we give methods for the synthesis of alkyl vinyl sulfoxides and sulfones from vinyl sulfides, which are readily synthesized by the vinylation of thiols [24]. They may therefore successfully compete with other previously described methods of synthesis, which are multistage processes based on the use of such toxic compounds as mustard gas derivatives [12, 15, 17, 23].

$$\begin{array}{c} CH_2 - CH_2 + RSH \longrightarrow HOCH_2CH_2SR \xrightarrow{H_2O_2} HOCH_2CH_2SOR \xrightarrow{H_2O_2} \\ & (SO_2) \end{array}$$

EXPERIMENTAL

All the vinyl sulfides were prepared by the vinylation of the corresponding thiols [24]. Peroxybenzoic acid was prepared by an improved modification [29] of Prilezhaev's method [28]. Concentrated hydrogen peroxide and peroxyacetic acid were prepared as described by Arbuzov [30].



of $CH_2 = CH - SO - CH_3 1$) in heptane

and 3) in alcohol; of $CH_2 = CH - SO -$

 C_2H_5 2) in heptane and 4) in alcohol.

The ultraviolet spectra were measured in heptane or alcohol solution with the aid of an SF-4 spectrophotometer (limit of measurement 220 m μ). Raman spectra were determined with the aid of an NSP-51 spectrograph. The positions of the lines were determined on the pure liquids, but the intensities were determined in carbon tetra-chloride solution. The unit of intensity was taken as one-hundredth of the integral intensity of the lines at 313 cm⁻¹ of carbon tetrachloride, the spectrum being excited by the mercury line at 4358 A.

Vinyl Sulfoxides

Ethyl Vinyl Sulfoxide. A 70% solution of hydrogen peroxide (2.7 ml, 0.105 mole) was added dropwise to a stirred mixture of 8.8 g (0.1 mole) of ethyl vinyl sulfide and 8 ml of acetone (cooled with snow and salt) at such a rate that the temperature of the reaction mixture did not exceed 5°. The mixture was stirred for ten hours at 0-5°, left for 35-40 hours at room temperature, and then heated for three hours in a water bath at 60-70° (after a preliminary addition of anhydrous Na₂SO₄). A qualitative test showed the absence of $H_2O_2^*$. Acetone and unoxidized vinyl sulfide were vacuum-evaporated (trap

surrounded by acetone and solid carbon dioxide). Distillation of the residue gave 8.0 g (77.4%) of ethyl vinyl sulfoxide; b.p. 75-76° (4 mm); n D^{20} 1.4920. After repeated fractionation the residue had: b.p. 54.2° (2 mm); n D^{20} 1.4900; d₄²⁰ 1.0422. Found: C 45.70; 45.70; H 7.87; 7.66; S 30.43; 30.67%. C₄H₈OS. Calculated: C 46.10; H 7.70; S 30.73%. By titration of the contents of the trap by the mercuric chloride method [31], 2.1 g (about 22%) of unchanged ethyl vinyl sulfide was found.

<u>Propyl Vinyl Sulfoxide.</u> This was prepared by the same method, but without heating toward the end of the experiment, from 10.2 g (0.1 mole) of propyl vinyl sulfide and 0.14 mole of H_2O_2 in the form of a 70% solution in 13 ml of acetone; yield 8.2 g (69.5%); b.p. 83° (8 mm); n_D^{20} 1.4870; d_4^{20} 1.0125. Found: C 50.57; H 8.74; 8.72; S 26.70; 26.72%. C₅H₁₀SO. Calculated: C 50.85; H 8.54; S 27.11%.

Butyl Vinyl Sulfoxide. This was prepared by the same method from 58 g (0.5 mole) of butyl vinyl sulfide and 0.55 mole of H_2O_2 as a 70% solution in 40 ml of acetone; yield 43 g (65.1%); b.p. 88-90° (6 mm); n D^{20} 1.4840; d_4^{20} 0.9891. Found: C 54.26; 54.26; H 8.77; 8.87; S 24.12; 24.32%. C₆H₁₂SO. Calculated: C 54.54; H 9.16; S 24.27%.

<u>2-Butoxyethyl Vinyl Sulfoxide</u>. This was prepared by the same method from 8.6 g (0.053 mole) of 2butoxyethyl vinyl sulfide and 0.055 mole of H_2O_2 as a 78% solution in 9 ml of acetone; yield 6.0 g (58.2% b.p. 113-114 (2 mm); n_D^{20} 1.4765; d_4^{20} 1.0138. Found: C 54.43; 54.23; H 9.28; 9.44; S 18.24; 18.24%). C₈H₁₆SO₂. Calculated: C 54.54; H 9.09; S 18.1%.

Methyl Vinyl Sulfoxide. By the same method, from 11 g (0.149 mole) of methyl vinyl sulfide (prepared in 32. $\overline{3\%}$ yield by the vinylation of methanethiol) and 4.29 ml(0.163 mole) of 78% H₂O₂ solution in 11 g of acetone we obtained 8.5 g of methyl vinyl sulfoxide; b.p. 49-50.5° (4 mm); n D²⁰ 1.4948. After repeated fractionations: b.p. 58.5-59° (6 mm); n D²⁰ 1.4951; d₄²⁰ 1.0876. Found: C 39.87; 6.71%. C₃H₆SO. Calculated: C 39.95; H 6.712%.

Phenyl Vinyl Sulfoxide. By the same method, from 14 g (0.103 mole) of phenyl vinyl sulfide and 3.8 g (0.11 mole) of H_2O_2 (as a 57% solution) in 25 ml of acetone we obtained 11.5 g (73.7%) of phenyl vinyl sulfoxide; b.p. 104-106° (2 mm); n_D^{20} 1.5774; after repeated fractionation: b.p. 132-133° (7 mm); n_D^{20} 1. 5869; d_4^{20} 1.1629. Found: C 62.97; 62.74; H 5.42; 5.54; S 21.01; 21.00%. C₈H₈SO. Calculated: C 63.14; H 5.30; S 21.07%.

From a series of experiments we obtained also small amounts of higher-boiling fractions (b.p. 126-128°) (3.5-4%), which later crystallized out and were found to be contaminated phenyl vinyl sulfone (m.p. after recrystallization, 66.5-67°).

^{*} An attempt to vacuum-evaporate solvent 24 hours after the start of the oxidation in one of the experiments on the synthesis of phenyl vinyl sulfoxide led to an explosion. Further experiments were prolonged for not less than 44-48 hours, and if unconsumed peroxide was present it was decomposed by the addition of MnO₂.

TABLE 4

Spectra of Vi	nyl S ulfoxide s	and Sulfones
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· ******	$-\omega(\text{cm}^{-1})$		1		λ max	
Substance	C=C	S-0	C · · C	s_0	որե	e max
CH ₂ =CHSOCH ₃				_	245	2300
CH ₂ =CHSOC ₂ H ₅	1601	1060 1032	26	25	247	2400
$CH_2 = CHSOC_3H_7$	1601	1070 1030	28	25	247	2600
CH2=CHSOC4H9	1602	1060 1030	30	25	247	2600
$C_2H_3SOC_2H_5*$		1068 1025		-	222**	1300
$CH_2 = CHSO_2C_2H_5$	1615	1126	32	48	220**	120
$CH_2 = CHSO_2C_3H_7$	1616	1128	26	38	220**	150
$CH_2 = CHSO_2C_4H_9$	1615	1128	30	40	220**	110
$C_2H_5SO_2C_2H_5^*$	*	1136		~100***		-
CH₂≖CHR	1642	-	30			

* Diethyl sulfoxide and sulfone were prepared by the oxidation of diethyl sulfide with hydrogen peroxide in acetone and their physical properties were in accord with data in the literature. The ultraviolet spectra of the sulfoxides were determined in heptane solution, and those of the sulfones were determined in ethanol solution.

**For these compounds the absorption coefficients given in the table are for the region of 220 m μ ; the maxima probably lie at shorter wavelengths.

***From data in [27].

TABLE 5

Oxidation of Ethyl Vinyl Sulfide with 28-30% H₂O₂ at 80°

Duration of heating (hr.)	Ethyl vinyl	Ethyl vinyl	Polymeric residue
	sulfoxide (%)	sulfone (%)	(% on weight)
1 2 10 60	38,5 45 1012 	10 21,2	22 28 57 80—90

TABLE 6

Oxidation of Ethyl Vinyl Sulfide (EVS) with H₂O₂ in t-Butyl Alcohol (40 ml)

Amount taken of			Reacti	on conditions	Yield of reaction products (%)	
EVS (moles)	H ₂ O ₂ (moles)	SeO ₂ (g)	total duration (hr.)	temp. in °C (time in hr.)	vınyl sulfoxide	vinyl sulfone
0,1 0,1 0,1	0,22 0,22 0,22	1,0 0,5 —	48 48 72	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	35 60	71 50 10

Vinyl Sulfones

Oxidation with H_2O_2 with Heating. a) Pyridine (0.44 ml) was added to 8.8 g (0.1 mole) of ethyl vinyl sulfide, and the mixture was stirred while 28.5 ml of 28% hydrogen peroxide (0.23 mole of H_2O_2) was added dropwise. On the addition of H_2O_2 the temperature remained in the range 20-40° and was then raised to 80°. The stirred reaction mixture was heated at this temperature for ten hours. First the homogenization of the reaction mixture was observed, and then an oily layer was precipitated on the bottom of the flask. The excess of H_2O_2 was decomposed by addition of MnO_2 , and water was vacuum-distilled off. The residue was diluted with chloroform and dried with sodium sulfate; chloroform was distilled off, after which we isolated 1.2 g of ethyl vinyl sulfoxide admixed with some sulfone [b.p. 62-79° (3 mm); n_D^{20} 1.4760] and 2.55 g (21.2%) of ethyl vinyl sulfone; b.p. 89-93° (3 mm); n_D^{20} 1.4628; d_4^{20} 1.1407. Found: C 40.33; 40.20; H 6.75; 6.74; S 26.76; 26.95%. C₄H₈SO₂. Calculated: C 40.00; H 6.60; S 26.60%.

The residue (5 g) was an undistillable resin, which was the only product in experiments with more prolonged heating. For the preparation of this polymeric substance in a purer form, in another experiment the low-boiling fractions were distilled off at $2 \cdot 10^{-2}$ mm. The residue was dried to constant weight in the same vacuum. Found: C 40.80; 40.90; H 6.99; 6.92; S 21.81; S 21.74%. (C₄H₈SO₂)n. Calculated: C 40.00; H 6.60; S 26.60%. In analysis the residue did not correspond to the polymer of the vinyl sulfone. The residue was soluble in dioxane and water, less soluble in chloroform, and almost insoluble in carbon tetrachloride. In solubility and appearance it corresponded to the product erroneously regarded by Reppe [6] as ethyl vinyl sulfone. The yields of sulfoxide, sulfone, and polymeric residue obtained under other conditions are given in Table 5.

b) When 4 g (0.035 mole) of butyl vinyl sulfide was heated with 9.3 g (0.07 mole of H_2O_2) of 27% hydrogen peroxide in presence of 0.4 ml of pyridine, we obtained 0.5 g of a mixture of butyl vinyl sulfoxide and sulfone (b.p. 93-100° (1 mm) and n_D^{20} 1.4712) and 2.03 g (39.8%) of butyl vinyl sulfone; b.p. 103-106° (3 mm); n_D^{20} 1.4640; d_4^{20} 1.0657. Found: C 48.86; 48.88; H 8.34; 8.43; S 21.67; 21.78%. C₆H₁₂SO₂. Calculated: C 48.58; H 8.20; S 21.63%. The polymeric residue, which was not investigated further, amounted to 2.0 g (50% on the weight of sulfide taken).

c) When 8.4 g (0.06 mole) of phenyl vinyl sulfide was oxidized for 60 hours with 15.7 g (0.23 mole) of hydrogen peroxide in the form of a 31% solution in presence of 0.26 ml of pyridine, we obtained 5.7 g (55.3%) of phenyl vinyl sulfone, m.p. 67.5-68° after two crystallizations from a mixture of benzene and petroleum ether.

Oxidation with Peroxy Acids. a) At -10° a solution of 0.12 mole of peroxybenzoic acid in 250 ml of chloroform was added to a solution of 5.2 g (0.058 mole) of ethyl vinyl sulfide in 50 ml of chloroform. The mixture was stirred at this temperature for four hours, and was then left at room temperature until a qualitative test for peroxide was negative (40 hours). Benzoic acid was neutralized by passage of a stream of dry ammonia at -10° , ammonium benzoate was filtered off, and solvent was vacuum-evaporated. Distillation of the residue gave 4.7 g (66%) of ethyl vinyl sulfone, b.p. 78-79° (1 mm) and n_D^{20} 1.4620. According to the ultraviolet spectrum (Fig. 1) the sulfone contained 1-2% of vinyl sulfoxide impurity.

b) A solution of 4.4 g (0.05 mole) of ethyl vinyl sulfide in 30 ml of ether was cooled to -20° , and 12.5 g (0.11 mole) of 67% peroxyacetic acid was added (the temperature was kept between -10° and 0°). The reaction mixture was stirred for 30 minutes with cooling and two hours at room temperature, after which the acetic acid was neutralized by the addition of 16.6 g of anhydrous potassium carbonate. After 40 hours the mixture was filtered off from the precipitate, which was washed repeatedly with ether; solvent was vacuum-evaporated, and we then obtained 1.2 g (10%) of a mixture of ethyl vinyl sulfoxide and sulfone, b.p. 65-86° (3 mm), and 3.9 g (73%) of ethyl vinyl sulfone: b.p. 91.5-96° (4 mm); n_D^{20} 1.4670.

Oxidation with H_2O_2 in Presence of SeO₂. a) Ethyl vinyl sulfide (8.8 g, 0.1 mole) was added to a solution of 1.0 g of SeO₂ in 40 ml of t-butyl alcohol (b.p. 79-81° n_D^{20} 1.3856). Hydrogen peroxide (11.5 g, i.e., 0.22 mole, of 75% solution) was diluted with cooling with 10 ml of t-butyl alcohol and added dropwise with stirring at such a rate that the temperature of the reaction mixture did not exceed 60-65° (external cooling). The mixture was then heated further for four hours at 60-70°. To free it from SeO₂, the reaction mixture was passed twice though a column of basic ion-exchange resin (e.g. EDE-10 II) *; the resin was washed with ether. The

^{*} It is somewhat less convenient to remove SeO_2 by passing the reaction mixture through a $CaCO_3$ column: for this purpose it is necessary first to distill off the alcohol and dilute the mixture with ether.

mixture was dried with sodium sulfate, and solvents were vacuum-distilled off. The only reaction product isolated was ethyl vinyl sulfone, which amounted to 8.5 g (71%); b.p. 87-88° (2 mm); n_D^{20} 1.4635 (residue in flask about 1 g). Table 6 shows the products of the oxidation of ethyl vinyl sulfide in t-butyl alcohol in presence of various amounts of SeO₂.

b) By the oxidation of 10.2 g (0.1 mole) of propyl vinyl sulfide with 11 ml of 75% H_2O_2 (0.22 mole of H_2O_2) in 40 ml of t-butyl alcohol in presence of 1.0 g of SeO_2 we obtained 8.8 g (66%) of propyl vinyl sulfone; b.p. 107-107.5° (5 mm); nD 1.4643; d_4^{20} 1.1060. Found: C 44.50; 44.71; H 7.48; 7.64; S 23.58; 23.54%. $C_5H_{10}SO_2$. Calculated: C 44.77; H 7.52; S23. 80%.

c) Under the same conditions, by the oxidation of 11.6 g (0.1 mole) of butyl vinyl sulfide with 13.0 g of 64% H_2O_2 (0.27 mole) in 40 ml of t-butyl alcohol in presence of 1 g of SeO₂ we obtained 8 g (54%) of butyl vinyl sulfone, b.p. 116-117° and n_D^{20} 1.4620.

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SUMMARY

1. The conditions were found for the selective oxidation of sulfur in vinyl sulfides with formation of sulfoxides and sulfones (50-70% yield).

2. The molecular refractions of vinyl sulfones and sulfoxides were determined; also, the character of the absorption in the ultraviolet and of the Raman spectra is discussed from the point of view of the electronic structures of the sulfoxide and sulfone groups.

3. The ultraviolet absorption spectra of vinyl sulfones were used as a criterion of purity.

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