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SYNTHESIS AND CONFIGURATIONAL ASSIGNMENT OF EPISULPHOXIDES[1]

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Abstract—A general procedure for the oxidation of olefin sulphides with perbenzoic acid to the corresponding episulphoxides has been established. The configuration of mono- and *cis*-disubstituted episulphoxides was determined with the aid of NMR spectra. By the analyses, based on the anisotropy effect of sulphinyl function and aromatic solvent induced shift (ASIS), we concluded that these episulphoxides obtained by our procedure have *anti*-configuration with respect to the substituent(s) and sulphinyl oxygen. Episulphoxides bearing an alkyl substituent and oxygen on the same side of the three-membered ring were quite unstable at room temp. Intramolecular hydrogen abstraction from the substituent followed by ring opening occurred and allylic thiolsulphinates were obtained as products.

IT IS WELL known that nearly all attempts to oxidize episulphides to the cyclic sulphones or sulphoxides resulted in ring opened products.[2] The only exception was noted by Dittmer and Levy in 1965,[3] who succeeded in the oxidation of dibenzoylstilbene sulphide to the corresponding sulphone and sulphoxide using H_2O_2. Later Hartzell and Paige[4] reported the isolation of pure ethylene episulphoxide by oxidizing ethylene sulphide with sodium metaperiodate[5] in MeOH. A recent report by Hardy *et al.*[6] also claims the successful oxidation of ethylene sulphide to the episulphoxide with t-BuOH-H_2O_2-V_2O_5 system. The Hartzell's procedure, however, seemed to us to have rather narrow applicability owing to the following reasons; (1) as commented by Hardy,[6] the high solubility of low molecular weight episulphoxides in reaction media makes it difficult to obtain the pure materials by extraction, and (2) some episulphoxides are too unstable to handle, *vide infra*, under the reaction conditions. In order to establish a more reliable method, we examined the reaction of episulphides with various oxidizing reagents including organic peracid, iodosobenzene,[7] t-butyl hypochlorite,[8] N_2O_4,[9] and H_2O_2. This paper describes the preparation of episulphoxides under very mild conditions in non-protic solvents. Another purpose of the present study was to investigate the stereochemistry of substituted episulphoxides by NMR which had never been discussed in previous papers.

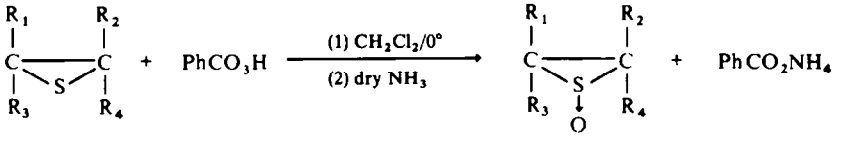
Synthesis

Propylene sulphide was chosen as a model compound for establishing the oxidizing conditions, because of its facile availability and stability.* A systematic investigation with above-mentioned reagents under various conditions proved that perbenzoic or *m*-chloreperbenzoic acid was the most suitable oxidizing reagent and CH_2Cl_2 a preferable solvent. Other organic peracids, such as 8% peracetic acid or 5% performic acid, and H_2O_2 gave ring opened products with incorporation of solvent molecules.

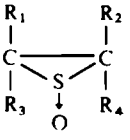
* While ethylene sulphide gradually polymerized during storage even in refrigerator, propylene sulphide was stable for several months.

The oxidation product obtained by treatment with iodosobenzene was a complex mixture containing the sulphoxide as minor component. No spot of the sulphoxide on TLC was detected with other oxidizing reagents.

Typically, to a solution of episulphide in CH_2Cl_2 was added a solution of equimolar perbenzoic acid in the same solvent below 0°. The oxidation was usually completed within a few min. as evidenced by potassium iodide-starch test. One of the problems of this procedure is the separation of episulphoxides from the simultaneously formed benzoic acid, as the latter is strongly bound to the former by hydrogen bonding. After several attempts, this difficulty was overcome by flashing dry NH_3 on the surface of the reaction. The precipitated ammonium benzoate was practically insoluble in CH_2Cl_2. Thus, mere filtration afforded essentially pure solution of episulphoxide in almost quantitative yield. When an excess of NH_3 was introduced into the reaction mixture, it was blown out with dry N_2 before filtration.



Yields of isolated pure episulphoxides and characteristic IR absorptions of S-O stretching are collected in Table 1. While lower members of the sulphoxides could be purified by distillation, 3-chloropropylene episulphoxide **4** and cyclohexene episulphoxide **5** were purified by column chromatography on silica. The crystalline episulphoxides with aromatic substituent(s) could easily be purified by recrystallizing from hexane-$CHCl_3$. Most of the episulphoxides listed in Table 1 were stable for several months when stored in a refrigerator, while they decomposed gradually at room temp and instantaneously at 100°. Both isomers of *cis*- and *trans*-stilbene episulphoxides decomposed foamingly, when heated *ca.* 10° higher than their m.ps. Tetraphenylethylene episulphoxide did not show any definite m.p., it turned pale yellow near 40° and melted at 220°, the m.p. of tetraphenylethylene.

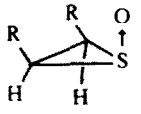
TABLE 1. SYNTHESIS OF EPISULPHOXIDES 

No.	R_1	R_2	R_3	R_4	Yield (%)	b.p. (or m.p.)	IR (cm^{-1})
1	H	H	H	H	77	53°/3	1060
2	CH_3	H	H	H	54	oil	1070,1050
3	CH_3	CH_3	H	H	41	oil	1080,1065
4	CH_2Cl	H	H	H	50	(20–22)	1065
5	$-(CH_2)_4-$		H	H	50	oil	1065,1050
6	Ph	H	H	H	52	(59–60)	1065
7	Ph	Ph	H	H	88	(79)	1065
8	Ph	H	H	Ph	90	(85)	1057
9	Ph	Ph	Ph	Ph	70	(~40 d)	1095

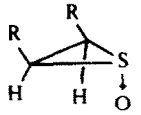
Some of the disubstituted episulphoxides could not be prepared under the above-mentioned conditions. For example, a neat sample of isobutene episulphoxide or *trans*-2-butene episulphoxide decomposed exothermically at room temp. Thus, all of the operations, *i.e.*, oxidation of the sulphides, removal of benzoic acid and evaporation of solvent, should be conducted below $-20°$. The isolated episulphoxides obtained as residual viscous oils were relatively stable at $-20°$ and could directly be subjected to NMR measurement by dissolving them in an appropriate precooled solvent. The structure of the decomposition product will be discussed in the later section.

Configuration of Substituted Episulphoxides

The geometrical position of the oxygen atom in ethylene episulphoxide has been determined by the complete analyses of NMR[10] and microwave[11] spectra. It is situated out of plane of the three-membered ring. Thus, mono- and *cis*-di-substituted episulphoxides are theoretically possible to exist in two configurations, *i.e.*, the one with substituent(s) and oxygen residing on the same side of the ring (*syn*-isomer, **A**) and the other with the each on the opposite side (*anti*-isomer, **B**).



A



B

The NMR spectrum of a pure sample of propylene episulphoxide **2** in CCl_4 is reproduced in Fig. 1. The one kind of Me doublet was observed in the spectrum and this is also the case for *cis*-2-butene episulphoxide **3**. These spectra strongly suggest

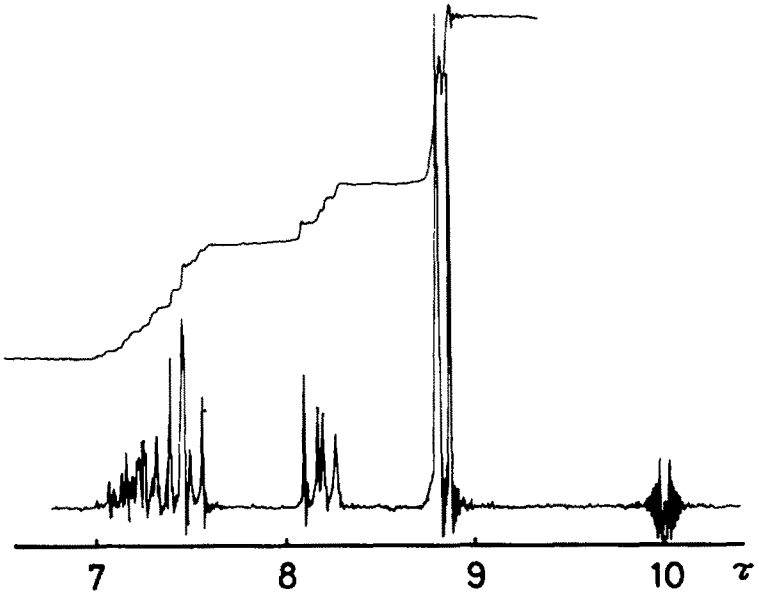


FIG 1. NMR spectrum of propylene episulphoxide in CCl_4.

that both episulphoxides are homogeneous with respect to the configuration. As the spectra of the crude sample of **2** or **3** measured before distillation were completely superimposable on those of the pure compounds, only one isomer, **A** or **B**, must be formed exclusively by our procedure. The organic peracid usually attacks from the less hindered side of the substrate to produce the less hindered oxidation product as the major isomer.[12] The observed stereoselectivity may, therefore, probably mean the exclusive formation of *anti*-isomer **B**. This assumption was confirmed by the following two standpoints of NMR analysis.

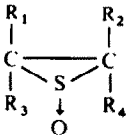
Chemical shifts studies. An acetylenic type anisotropy and a proximity effect of the S-O bond in cyclic systems have been well documented.[13] Thus, in certain six-,[14] five-,[15] and four membered[16] ring sulphoxides, a β-hydrogen which is *syn* to the S-O bond suffers from a pronounced deshielding effect, while a β-hydrogen which is *anti* to the S-O, *i.e.*, *syn* to the lone pair of the sulphinyl sulphur, suffers from a shielding effect. In order to examine the applicability of this chemical shift difference to the assignment of stereochemistry to our three-membered ring, we compared the chemical shifts of the same type protons in substituted episulphoxides, which were situated on either *syn* or *anti* side of the S–O bond, with those of parent sulphide.

The chemical shifts of Me protons in isobutene sulphide and *trans*-2-butene sulphide were observed as singlet at τ 8·41 and as doublet at 8·55 respectively. When these sulphides were transformed to the corresponding episulphoxides, two Me's in each compound became non-equivalent and showed different chemical shifts. The Me protons in isobutene episulphoxide were observed as two sharp singlets at τ 8·23 and 8·75, and those in *trans*-2-butene episulphoxide as two doublets at 8·35 and 8·72. Clearly, one Me signal shifted upfield and the other downfield as compared with those of parent sulphide. These observations may validate the applicability of the S–O anisotropy rule to the three-membered ring system, and the upfield signals were assigned to Me protons *anti* to the S–O bond and the downfield ones *syn* to the S–O. The assignments were finally confirmed by solvent shift studies which will be given in the next section.

The above-mentioned change of chemical shifts induced by S–O anisotropy may be a useful tool in determinging the configuration of mono- and *cis*-di-substituted episulphoxides. The NMR parameters of substituted episulphoxides and their parent sulphides are collected in Table 2. The observed chemical shift of Me protons in propylene episulphoxide **2** was 30 Hz higher than that of propylene sulphide. A similar upfield shift was also noted for the protons of substituents in *cis*-disubstituted episulphoxides, **3** and **5**. From the previous discussion, these upfield shifts may mean that the substituent(s) and sulphinyl oxygen reside on the opposite side of the ring and, therefore, the oxidation products have *anti*-configuration.

One final comment on the anisotropy of the S–O bond is needed. Although a remarkable upfield or downfield shift of β-hydrogen in a rigid system depending on the direction of S–O bond was noted in many cases, the same behaviour could not be necessarily observed for the hydrogens directly attached to the episulphoxide ring. For example, chemical shifts of methine protons in episulphoxides **2** and **3** and methylene protons in **10** were almost the same as those of corresponding episulphides. Therefore, we believe that shielding and deshielding effect of the S–O bond are compensating each other at these hydrogens. In this connection, it is quite interesting to know that two different ring protons in **10** appear as a sharp singlet at 7·73, while

TABLE 2. CHEMICAL SHIFTS (τ) OF SUBSTITUTED EPISULPHIDES AND EPISULPHOXIDES



	Substituents				Episulphides in CCl_4				Episulphoxides in CCl_4				Episulphoxides in PhH				$\Delta = (\tau)_{PhH} - (\tau)_{CCl_4}$			
No.	R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4
1	H	H	H	H	7·73	7·73	7·73	7·73	8·08	8·08	7·58	7·58	9·16	9·16	8·23	8·23	1·08	1·08	0·65	0·65
2	CH_3	H	H	H	8·52	8·00	7·21	7·62	8·82	8·21	7·21	7·46	9·62 9·33	9·04 8·70	7·71 7·56	7·95 7·79[a]	0·80 0·51	0·83 0·49	0·50 0·35	0·49 0·33
3	CH_3	CH_3	H	H	8·55	8·55	7·12	7·12	8·76	8·76	7·07	7·07	9·51	9·51	7·44	7·44	0·75	0·75	0·37	0·37
4	$ClCH_2$	H	H	H	6·89 6·46	7·78	6·89	7·46	~6·8 ~6·2	7·86	~6·8	7·22	~7·7 ~7·3	8·76	~7·3	7·82	~0·9 ~1·1	0·90	~0·5	0·60
5	$-(CH_2)_4-$		H	H	8·60 (β)	7·87 (α)	6·95	6·95	8·96 (β)	7·85 (α)	6·96	6·96	9·54	8·50	7·26	7·26	0·58 (β)	0·65 (α)	0·30	0·30
6	Ph	H	H	H	2·84	7·55	6·30	7·29	~2·9	7·29	6·03	6·99	—	8·06	6·41	7·53	- -	0·77	0·38	0·54
7	Ph	Ph	H	H	2·99	2·99	5·75	5·75	~2·8	~2·8	5·49	5·49[b]	—	—	5·94	5·94	—	—	0·45	0·45
8	Ph	H	H	Ph	2·79	6·24	6·24	2·79	~2·7	6·00	5·73	~2·7[b]	—	6·65	6·08	—	—	0·65	0·35	—
10	CH_3	H	CH_3	H	8·41	7·74	8·41	7·74	8·75	7·73	8·23	7·73[c]	9·33	8·50	8·60	8·33[d]	0·58	0·77	0·37	0·60
11	CH_3	H	H	CH_3	8·55	7·50	7·50	8·55	8·72	7·82	7·52	8·35[e]	9·32	8·62	8·08	8·65[d]	0·60	0·80	0·56	0·30

[a] in PhCl at +28°
[b] in $CDCl_3$ at +28°
[c] in $CDCl_3$ at −38°
[d] in PhCl at −27°
[e] in $CDCl_3$ at −50°

the one is *anti* and the other is *syn* to the S–O bond. The accidental coincidence of the chemical shifts was confirmed by the following ways. When we added a small amount of benzoic acid to the NMR sample solution of **10**, the methylene signal splitted to an AB quartet, τ 7·60 and 7·74, J_{AB} = 3·7 Hz. This AB quartet coalesced again when the added acid was removed by treatment with dry NH_3 as described in the synthesis section. The chemical shift of protons in cross proximity with sulphinyl oxygen usually shows a downfield shift in strong acidic media as compared with that in a non-polar solvent.[17] Thus, we assigned the lower and the higher field signals of the AB quartet to the ring protons *syn* and *anti*, respectively, to the S–O bond.

Solvent-shift studies. Aromatic solvent-induced shifts (ASIS) has successfully been applied to the assignment of stereochemistry to polar molecules, especially, to cyclic sulfoxides.[18] The ASIS is based on a concept of coordination between aromatic systems and the electron-deficient site of a polar solute molecule. To visualize this, Ledaal[19] has recently proposed a model of benzene-solute collision complexes with the positive end of the dipole of the polar solute being located nearest and the negative end farthest away along the sixfold axis of the benzene molecule. According to this model, a remarkable shielding for the substituents and hydrogens *anti* to the S–O bond of the episulphoxides by aromatic solvent is expected. The chemical shift differences of various protons in the episulphoxides measured in CCl_4 and benzene are summarized in Table 2. Evidently, most protons suffer from shielding in benzene than in CCl_4. However, a detailed inspection of the solvent-shift values revealed that protons residing on the opposite side of the sulphinyl oxygen were more shielded than similar protons on the same side. For example, each of the methylene protons in propylene episulphoxide exhibited different solvent-induced shifts and the one with larger shift value corresponded to the proton assigned to be *anti* to the S—O bond by the magnitude of chemical shift. These data also support the aforementioned assignment of stereochemistry to the mono- and *cis*-di-substituted episulphoxides.

Thermal Decomposition of Substituted Episulphoxides

Ethylene episulphoxide is known to decompose at 100° to unstable sulphur monoxide and ethylene[4] and the reaction has been utilized as an effective source of sulphur monoxide.[20] On the other hand, isobutene episulphoxide **10** decomposes exothermically at room temp. In order to regulate the vigorous decomposition, the episulphoxide was dissolved in $CHCl_3$ and kept overnight at 0 ~ 5°. The completion of the reaction and the formation of a new product were ascertained by TLC. The decomposition product obtained from **10** exhibited characteristic IR absorptions due to sulphinyl and terminal methylene groups and NMR absorptions attributable

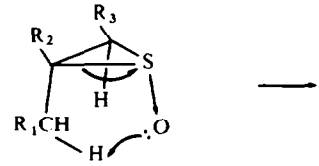
TABLE 3. ALLICIN AND ITS HOMOLOGUES. RS(O)SR

No.	R	Yield (%)*	IR (cm^{-1}) C=C—H	IR (cm^{-1}) S–O
14	CH_2=C(CH_3)CH_2—	86	1650, 900	1080
15	CH_2=CHCH(CH_3)—	83	1650, 925	1085
16	$(CH_2)_4$CH=C—CH_2—	63	1650	1075
17	CH_2=CHCH_2—	10	1635, 990, 930	1090

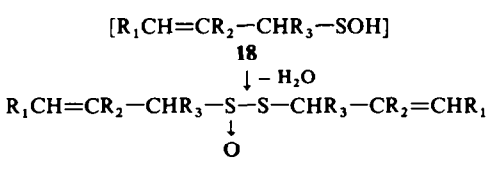
* based on used episulphide

to two different allylic Me's and methylenes, at τ 8·11, 8·16 and 6·34, 6·37, respectively. From these spectra and elemental analyses, we assigned structure **14** to the product (Table 3). The assignment was confirmed by chemical degradation to methallyl mercaptan with LAH and by an independent synthesis of the product from methallyl disulphide. The formation of allylic thiolsulphinate **14** may be rationalized by assuming an intramolecular hydrogen transfer from the substituent *syn* to the S–O bond to the oxygen and subsequent dehydrative dimerization[21] of the resulting sulphenic acid **18**, as shown in the following scheme.*

Similarly, *trans*-2-butene episulphoxide **11** and 1-thiaspiro-[2,5]octane-1-oxide **12**



10: $R_1=R_3=H, R_2=CH_3$
11: $R_1=R_2=H, R_3=CH_3$
12: $R_1,R_2=-(CH_2)_4-, R_3=H$
13: $R_1=R_2=R_3=H$



were also unstable at room temp. even in solution and were transformed spontaneously to the corresponding allylic thiolsulphinates **15** and **16**, respectively, in good yield. Both thiolsulphinates were characterized by spectra and analyses.

An intramolecular β-elimination of sulphoxides to afford olefins is a well known reaction.[23] While it is necessary to heat to more than 100° to induce the elimination of acyclic sulphoxides, our three-membered system eliminates spontaneously at room temp. The assisting factors for the ease of this elimination will be found in the relief of strain by opening of the three-membered ring and in the presence of hydrogen forced to come to the near proximity of oxygen by the rigidity of the cyclic system.

Although we have no definitive evidence for the intramolecular nature of the hydrogen abstraction, the presence of hydrogen on α-carbon of the ring substituent which is *syn* to the S–O bond is essential for the formation of allylic thiolsulphinates. In sharp contrast with these episulphoxides, mono- and *cis*-di-substituted ones have no available hydrogen for abstraction. Thus, the thermolysis of these compounds afforded only olefins and sulphur monoxide.

In this connection, the oxidation product of propylene sulphide with sodium metaperiodate is quite interesting. The NMR spectrum of crude material obtained by Hartzell's procedure,[24] exhibited a characteristic absorption due to terminal vinyl at τ 4·0 ~ 5·0, besides those of propylene episulphoxide **2**. The TLC of the material also indicated the presence of two substances, one of which showed identical R_f value with that of **2**. The separation of the two was performed by column chromatography on silica with benzene-$CHCl_3$ (1 : 1). The structure of the second substance was proved to be 2-propenethiol 2-propenesulphinate **17**, *i.e.* allicin,[25] a famous antibacterial principle of *Allium sativum*, by spectra. The isolated yield of **17** was *ca.*

* Episulphoxide is an isoelectronic counterpart of perepoxide which is now assumed to be a strong candidate for the intermediate in the formation of hydroperoxides from olefins and singlet oxygen.[22] The similarity between the reaction scheme described here and that proposed for the reaction of $^1O_2$ is quite interesting.

10% based on the used propylene sulphide. The by-production of **17** may easily be understood by the above-mentioned intra-molecular elimination as follows. Sodium metaperiodate attacked propylene sulphide less stereoselectively as compared with organic peracid. Thus, in this case, a measurable amount of *syn*-episulphoxide **13** was produced as a minor component, although the *anti*-episulphoxide, **2**, was always a major one. The *syn*-isomer must be unstable at room temp, and be transformed to thiolsulphinate **17** during the work-up process.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. The IR spectra were recorded on a Hitachi–Perkin–Elmer Infracord 337 grating spectrophotometer. The NMR spectra were recorded by Mr. K. Sato on Varian HA-100 spectrometer using TMS as an internal standard. Microanalyses were carried out in the microanalytical laboratory of our Center under the direction of Mr. M.Yamamoto. TLC (silical gel) was employed routinely and developed with hexane-$CHCl_3$ (7:3) and visualized with iodine vapour. All starting episulphides were prepared by known methods.[2, 26]

Ethylene episulphoxide (**1**). The following preparation illustrates a general procedure for the oxidation of episulphides. To a stirred solution of 6 g (0·1 mole) of ethylene sulphide in CH_2Cl_2 (200 ml), maintained at $-10°$ in Dry Ice-EtOH bath, was added gradually 200 ml of 0·5 molar solution of perbenzoic acid in CH_2Cl_2. The consumption of peracid was checked by spotting on moist iodine-starch paper. Usually, oxidation was completed withing a few min after the addition of peracid and the TLC of the mixture indicated the presence of episulphoxide (R_f = 0·6) as sole product. On the surface of the mixture, dry NH_3 was introduced directly for several min. Excess NH_3 was expelled by bubbling N_2 into the mixture. All of the above operations were conducted below $-10°$. The precipitated ammonium benzoate was filtered and the filtrate concentrated under reduced pressure to afford a colourless liquid. Distillation of the residual oil gave **1** (5·5 g, 77%); b.p. 53°/3 mm. (Found: S, 42·03. C_2H_4OS requires: S, 42·12%).

Propylene episulphoxide (**2**). In similar manner, 0·74 g (0·01 mole) of propylene sulphide dissolved in CH_2Cl_2 (100 ml), was oxidized with 20 ml of 0·5 molar perbenzoic acid soln at $-20°$. After work-up as above the residual oil was distilled under high vacuum (10^{-3}–10^{-4} mm) at room temp. The distillate was collected in a trap cooled by liquid N_2. Pure episulphoxide **2** (0·49 g, 54%) was obtained as a colourless liquid within 30 min. Although TLC of the residual oil in the still indicated the presence of **2** as a major component, attempted distillation of the oil under the same pressure was proved not to be effective due to its high viscosity. NMR (Fig 1); $J_{1,3}$* = 6·5, $J_{2,3}$ = 9·0, $J_{2,4}$ = 6·0, $J_{3,4}$ = 10·0 Hz. (Found: C, 39·53; H, 6·79; S, 35·34. C_3H_6OS requires: C, 39·97; H, 6·71; S, 35·57%).

cis-2-Butene episulphoxide (**3**). The oxidation of *cis*-2-butene sulphide (0·84 g, 0·01.mole) with equimolar perbenzoic acid was carried out as above. Distillation of the crude product at 10^{-3}–10^{-4} mm gave **3** (0·34.g, 41%) as a slightly viscous oil which was collected in a trap cooled by Dry Ice-acetone bath. NMR parameters are given in Table 2. The splitting of Me signal was 7·0.Hz. (Found: C, 46·03; H, 7·73; S, 30·66. C_4H_8OS requires: C, 46·12; H, 7·74; S, 30·78%).

3-Chloropropylene episulphoxide (**4**). The oxidation of 3-chloropropylene sulphide (1·09.g, 0·01.mole) with equimolar perbenzoic acid was carried out as above at -20– $-30°$. The crude product was a yellow viscous oil and could not be purified by distillation. Thus, the oil was purified by column chromatography on silica. Elution with C_6H_6–$CHCl_3$ (1:1) afforded **4** (0·63 g, 50%) as a colourless oil, which solidified on cooling, m.p. 22–23°. (Found: S, 25·57. C_3H_5ClOS requires: S, 25·74%).

Cyclohexene episulphoxide (**5**). Cyclohexene sulphide (1·14 g, 0·01 mole) was oxidized as above at -30– $-40°$. Purification of crude product was performed by column chromatography on silica. Elution with C_6H_6-$CHCl_3$ (1:1) yielded pure **5** (0·65 g, 50%) as a colourless viscous oil. (Found: S, 24·56. $C_6H_{10}OS$ requires: S, 24·63%).

Styrene episulphoxide (**6**). Styrene sulphide (1·36 g, 0·01 mole) in CH_2Cl_2 (100.ml), was oxidized as above at $-30°$. After treatment with dry NH_3 and N_2 at the same temp, the mixture was filtered and the filtrate concentrated *in vacuo* at $-20°$. Although the crude product obtained as a colourless crystals was almost pure, the IR spectrum indicated the presence of ammonium benzoate as a minor contaminant. Recrystallization of the product from ether–petroleum ether (b.p. 40–50°) afforded pure **6** (0·79 g, 52%), m.p. 52–53°. NMR: $J_{2,3}$ = 10, $J_{2,4}$ = 8, $J_{3,4}$ = 10 Hz. (Found: C, 62·26; H, 5·33; S, 21·13. C_8H_8OS requires: C, 63·13; H, 5·30; S, 21·06%).

* $J_{1,2}$ refers to coupling constant between protons on substituents R_1 and R_2.

cis-Stilbene episulphoxide (7). *cis*-Stilbene sulphide (200 mg, 0·94 mmol) in $CHCl_3$ (50 ml) was oxidized with equimolar perbenzoic acid dissolved in $CHCl_3$ (10 ml) at $-10°$. Post-treatments were carried out in the same manner as before. Recrystallization of crude product from hexane-$CHCl_3$ (6:4) gave **7** (188 mg, 88%) as colourless crystals. Further purification by treatment with activated charcoal in $CHCl_3$ and recrystallization from the same solvent afforded an analytically pure sample, m.p. 79°. (Found: C, 73·58; H, 5·47; S, 13·85. $C_{14}H_{12}OS$ requires: C, 73·65; H, 5·30; S, 14·04%).

trans-Stilbene episulphoxide (**8**). This was prepared in the same manner as the *cis*-isomer. The oxidation of *trans*-stilbene sulphide (210 mg, 1 mmol) and recrystallization of crude product from hexane-$CHCl_3$ (6:4) yielded **8** (205 mg, 90%), m.p. 85°. NMR: $J_{2,3} = 11$ Hz. (Found: C, 73·46; H, 5·38; S, 14·10. $C_{14}H_{12}OS$ requires: C, 73·65; H, 5·30; S, 14·04%).

Tetraphenylethylene episulphoxide (**9**). Tetraphenylethylene sulphide (360 mg, 1 mmol) in CH_2Cl_2 (50 ml) was oxidized as above at $-20°$. As the reaction proceeded rather sluggishly, it took several hrs for the complete disappearance of peracid. The crude product was recrystallized from hexane-$CHCl_3$ at $-10°$ to give pure **9** (260 mg, 70%) as colourless crystals. This episulphoxide is thermally labile. Therefore, characteristic S–O stretching of the compound at 1095 cm^{-1} diminished gradually during the IR measurement. (Found: C, 82·02; H, 5·45; S, 7·5. $C_{26}H_{20}OS$ requires: C, 82·07; H, 5·30; S, 8·43%).

Isobutene episulphoxide (**10**). To a stirred soln of isobutene sulphide (2·2 g, 0·025 mole) in CH_2Cl_2 (100 ml) cooled to $-30°$ was added dropwise an equimolar amount of perbenzoic acid in CH_2Cl_2. After ascertaining the consumption of peracid, the mixture was cooled to $-40°$. Flushing of dry NH_3 on the surface of the mixture resulted in precipitation of ammonium benzoate as fine crystals. The precipitate was filtered off as quickly as possible using a precooled glass filter at $-20°$ and the filtrate treated with activated charcoal. Concentration of the solvent *in vacuo* at $-20°$ afforded a colourless oil, which was immediately dissolved in precooled ($-50°$) $CDCl_3$ or chlorobenzene and was submitted for NMR analyses at the temperatures given in Table 2.

trans-2-Butene episulphoxide (**11**). The oxidation of *trans*-2-butene sulphide was carried out as described above for isobutene sulphide. The crude product obtained by the evaporation of the solvent was immediately dissolved in a precooled suitable solvent for NMR analyses.

Thermolysis of isobutene episulphoxide. The crude isobutene episulphoxide prepared from 0·88 g (0·01 mole) of isobutene sulphide was dissolved in $CHCl_3$ (50 ml) and kept at 0–5° in a refrigerator. The mixture became turbid after 24 hr and TLC of the mixture indicated the formation of a new product. Concentration of the mixture *in vacuo* at room temp afforded 0·82 g (86% based on the used isobutene sulphide) of 2-methyl-2-propenethiol 2-methyl-2-propenesulphinate, **14**. (Found: S, 33·61. $C_8H_{14}OS_2$ requires: S, 33·69%). IR (neat): 1080, 900 cm^{-1}; NMR: τ (CCl_4) 5·0 m 1H, 5·1 m 1H, 6·34 s 2H, 6·37 m 2H, 8·11 s 3H, 8·16 s 3H.

Reduction of thiolsulphinate **14** *with LAH.* To a stirred soln of 1·52 g (0·04 mole) of LAH in dry ether (90 ml) was added a soln of 2·28 g (0·012 mole) of thiolsulphinate, **14**, in 50 ml of the same solvent at room temp. After refluxing for ½ hr, the excess LAH was decomposed by successive addition of water (5 ml) and 15% sulphuric acid (20 ml). The etheral layer was separated and the aqueous layer extracted three times with ether. The combined organic layer was dried ($MgSO_4$) and evaporated. Distillation of the residual oil gave 2-methyl-2-propenethiol (1·07 g, 51%), b.p. 91–92°. NMR: τ (CCl_4) 5·17 bs 1H, 5·32 bs 1H, 6·94 d 2H, 8·15 s 3H, 8·77 t 1H.

According to the method of Bost *et al.*,[27] the mercaptan was converted to solid sulphide by treatment with 2,4-dinitrochlorobenzene. Recrystallization of the crude product from EtOH gave pure 2-methyl-2-propenyl 2,4-dinitrophenyl sulphide, m.p. 84°. (Found: C, 47·17; H, 3·93; N, 11·08; S, 12·49. $C_{10}H_{10}N_2O_4S$ requires: C, 47·05; H, 4·34; N, 10·97; S, 12·56%).

Alternate synthesis of 2-methyl-2-propenethiol 2-methyl-2-propenesulphinate. Dimethallyl disulphide was prepared according to the reported method[28] in 68% yield, b.p. 73–76°/2·5 mm. To a soln of the dilsulphide (0·435 g, 2·5 mmol) in CH_2Cl_2 (30 ml) cooled in an ice-water bath was added slowly an equimolar perbenzoic acid in CH_2Cl_2 (10 ml). The by-product, benzoic acid was removed by treatment with dry NH_3 in the same manner as developed for the synthesis of episulphoxides. The crude product weighed 255 mg (54%) and showed identical IR and NMR spectra with those of thermolysis product **14**.

Thermolysis of trans-2-butene episulphoxide. The decomposition of *trans*-2-butene episulphoxide (prepared form 0·88 g of the sulphide) in the same manner as described for isobutene episulphoxide resulted in the formation of a diastereomeric mixture of 1-methyl-2-propenethiol 1-methyl-2-propenesulphinates (780 mg, 83% based on the used sulphide). The crude product was purified by treatment with activated

charcoal in $CHCl_3$. (Found: S, 33·96. $C_8H_{14}OS_2$ requires: S, 33·69%). NMR: τ (CCl_4) 4·0 ~ 5·0 m 6H, 5·95 bd 1H, 6·40 quintet 1H, 8·28 bd 3H, 8·53 d 3H.

Thermolysis of 1-thiaspiro[2,5]octane-1-oxide. To a stirred soln of 0·51 g (4 mmol) of 1-thiaspiro[2,5]-octane in 50 ml of ether cooled to −30° was added dropwise an equimolar amount of *m*-chloroperbenzoic acid dissolved in ether (20 ml). After the same post-treatment as before with NH_3 and N_2 the mixture was filtered and the filtrate left overnight in a refrigerator. Concentration of the mixture under reduced pressure afforded a colourless oil, purified by column chromatography on silica. Elution with $CHCl_3$ yielded the corresponding allylic thiolsulphinate, **16**, (0·34 g, 62·5%). (Found: S, 23·66. $C_{14}H_{22}OS_2$ requires: S, 23·71%).

Oxidation of propylene sulphide with sodium metaperiodate. To a stirred soln of 9 g of $NaIO_4$ in H_2O (100 ml) was added slowly a soln of 2·5 g of propylene sulphide in MeOH (100 ml) at 0–5°. After additional stirring for 2 hr, the cold mixture was filtered and the aqueous filtrate repeatedly extracted with 30 ml portions of $CHCl_3$. The combined extracts were dried ($MgSO_4$), followed by concentration. The TLC of the residual oil indicated the presence of two products. Each of the components was isolated by column chromatography on silica. Elution with $CHCl_3$-benzene (1:1) yielded propylene episulphoxide (0·94 g, 30%) as the first eluting substance and the unstable thiolsulphinate **17**, allicin, (0·27 g, 10% based on used propylene sulphide) as the second.

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