Tetrahedron Letters No.29, pp. 2461-2464, 1969. Pergamon Press. Printed in Great Britain.

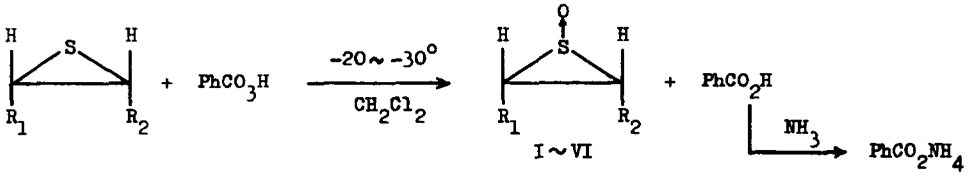
ISOLATION AND CHARACTERIZATION OF EPISULFOXIDES

Kiyosi Kondo, Akira Negishi and Masaru Fukuyama
Sagami Chemical Research Center
3100 Onuma, Sagamihara, 229 JAPAN

(Received in Japan 30 April 1969; received in UK for publication 15 May 1969)

In a recent communication, Hartzell and Paige (1) reported that the sodium metaperiodate oxidation of ethylene episulfide in aqueous methanol gave the corresponding episulfoxide. This method, however, afforded impure materials in low yields when applied to the syntheses of substituted ones and the identification of the products was rather obscure. We now wish to describe the isolation and spectroscopic characterization of several episulfoxides which were obtained by perbenzoic acid oxidation of episulfides in non-aqueous solvents.

A solution of episulfide in methylene chloride was treated with an equimolar amount of perbenzoic acid (2) at -20 to -30°. Usually, oxidation was completed in a few minutes. The simultaneously formed benzoic acid was transformed to its ammonium salt by flashing dry ammonia on the surface of the reaction mixture and easily removed by filtration. Evaporation of the solvent afforded almost pure episulfoxides, which were purified by appropriate methods depending on the nature of the products (vide infra).



Yields, bp. or mp., S-O stretching frequencies, and analyses of the pure episulfoxides are listed in Table I. Usual distillation of crude ethylene episulfoxide (I) gave the pure material in 77% yield, which was the highest value ever reported. Propylene episulfoxide (II) and cis-2-butene episulfoxide (III) could not be distilled without

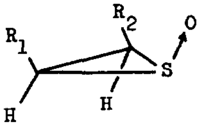
Table I

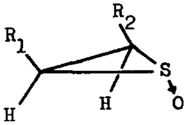
Episulfoxides Obtained by Perbenzoic Acid Oxidation of Episulfides

Compd. No.	R_1	R_2	Yield %	Bp.(mp.) °C/mm.(°C)	ν_{S-O} cm^{-1}	Analysis (%) Found S	Calcd. S
I	H	H	77	53/3	1060	42.03	42.12
II	H	CH_3	54	oil	1070, 1050	35.34	35.57
III	CH_3	CH_3(cis)	41	oil	1080, 1065	30.66	30.78
IV	$-(CH_2)_4-$		50	oil	1065, 1050	24.56	24.62
V	H	CH_2Cl	50	(20-22)	1065	25.57	25.74
VI	H	C_6H_5	52	(59-60)	1065	21.13	21.06

decomposition. *However, molecular distillation* ($< 10^{-4}$ *mm.*) *at room temperature gave pure products.* Cyclohexene episulfoxide (IV) and 3-chloropropylene episulfoxide (V) were purified by column chromatography on silica gel using benzene-chloroform as an eluant. Styrene episulfoxide (VI) was crystalline in crude state and recrystallized from dichloromethane-pentane to give an analytically pure sample. In all cases examined, the crude products showed essentially identical ir and nmr spectra with those of purified ones. Thus, the yields recorded in Table I mean the minimum values and represent the pure products in hand.

Episulfoxides bearing one substituent or two vicinal substituents at cis position can assume *two configurations, i.e. syn- and/or anti-configurations, A and B, respectively, in monomeric state.*


A


B

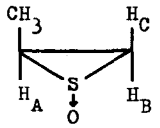
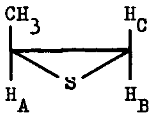
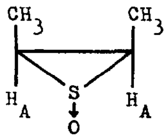
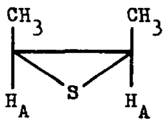
The nmr spectra would be a useful tool to distinguish these two configurations. In the case of ethylene episulfoxide, a typical A_2B_2 pattern centered at τ 8.02(2H) and 7.61(2H) was observed. Thus, episulfoxides are presumed to exist in a fixed configuration and not in a dynamic equilibrium between A and B on the nmr time scale. Meanwhile, for propylene and cis-2-butene episulfoxides (II, III), only one kind of methyl doublet was observed. This strongly suggests that both episulfoxides are of only one configuration and not a mixture of A and B.

In order to make a choice between the two, a comparison of the chemical shifts of substituent(s) in episulfoxides II and III with those of the parent episulfides is desirable. As summarized in Table II, the methyl hydrogen peaks in II and III are shifted upfield significantly with respect to the corresponding peaks for the episulfides. According to a number of data accumulated (3) on the anisotropy effect of S-O bond, protons situated in the close proximity of the S-O bond are generally deshielded, while protons in the opposite side of the bond (lone pair side) suffer shielding effect, as compared with the same protons of the parent sulfide (4). If this rule is applicable to the cyclic three-membered system, the episulfoxides II and III are considered to have the anti-configuration (B). Considering the steric hindrance of substituent(s) in the peracid oxidation, the preferential formation of the anti-isomer would also be expected.

One way to ascertain the above mentioned assignment of configuration is to examine the chemical shifts of protons forced to come to the same side of the S-O bond. For this purpose, syntheses of isobutene episulfoxide (VII) and trans-2-butene episulfoxide (VIII) have been attempted. These two sulfoxides were so unstable to be isolated in pure state

Table II

Chemical Shift Values (τ) of Episulfoxide and Episulfide (6)

	H_A 7.26(m) H_B 7.46(q) H_C 8.18(q) CH_3 8.82(d)		H_A 7.23(m) H_B 7.63(d) H_C 8.01(d) CH_3 8.50(d)
	H_A 7.11(m) CH_3 8.77(d)		H_A 7.15(m) CH_3 8.56(d)

that neat sample decomposed exothermically at room temperature (5). It was, however, possible to prepare chloroform solutions of these sulfoxides, when the oxidation of sulfides and removal of benzoic acid were performed below -10°. Both episulfoxides showed two kinds of methyl signal of equal intensity, at τ 8.26(s) and 8.75(s) for VII at -38°, and τ 8.36(d) and 8.73(d) for VIII at -50° (6). The corresponding methyl protons in isobutene episulfide and *trans*-2-butene episulfide absorbed at τ 8.41(s) and 8.55(d), respectively. Clearly, one methyl peak shifted upfield and the other downfield, as the result of the transformation from the sulfide to the sulfoxide.

The above observation may validate the applicability of the S-O anisotropy rule to our system, and we believe that the steric control of substituent(s) plays an important role in the exclusive formation of *anti*-episulfoxides (B) from mono- and *cis*-disubstituted episulfides.

The authors wish to thank Dr. G. Tsuchihashi for helpful discussions and Mr. K. Sato for technical assistance.

REFERENCES AND FOOTNOTES

1. G. E. Hartzell and J. N. Paige, *J. Am. Chem. Soc.* **88**, 2616 (1966); *J. Org. Chem.* **32**, 459 (1967). For other specific episulfoxide, see D. C. Dittmer and G. C. Levy, *J. Org. Chem.* **30**, 636 (1965).
2. A perbenzoic acid solution in methylene chloride was titrated immediately before use.
3. For leading reference, see A. B. Foster, T. D. Inch, M. H. Qadir and J. M. Webber, *Chem. Comm.* 1086 (1968).
4. For example, Webber and coworkers (3) have shown in a series of 1,4-oxathiane derivatives that the axial proton on 6-position is deshielded by an axial S-O group and shielded by an equatorial S-O group.
5. The structure of the decomposition products will be disclosed in full paper.
6. The nmr spectrum was measured on a Varian HA-100 spectrometer in chloroform solution using TMS as an internal standard.
   s in parentheses for singlet, d for doublet, q for quartet and m for multiplet.