Table I. Tryptophan Content of Representative Proteins

| | Mol wt | No. of tryptophan residues per molecule Lit. | Detd by MCD | No. of tyrosine residues per molecule |
|---|---|---|---|---|
| Lysozyme (hen egg white) | 14,300 | 6[c] | 5.92 | 3 |
| Albumin (bovine) | 67,000[a,b] | 1.85[b] | 1.93 | 17.9 |
| Tryptophan synthetase α chain (*E. coli*) | 28,900 | 0[c,d] | 0 | 7 |

[a] Molecular weight as indicated by the supplier Mann Research Laboratories as compared to 64,000 given by footnote *b*. [b] G. R. Tristam and R. H. Smith, *Advan. Protein Chem.*, **18**, 227 (1963). [c] M. O. Dayhoff and R. V. Eck, "Atlas of Protein Sequence and Structure," Vol. 4, The National Biochemistry Research Foundation, Silver Spring, Md, 1969. [d] Reference 8.

Finally it should be pointed out that the sensitivity of our method is comparable to the spectrophotometric technique, and depending on the tryptophan content protein concentrations of 0.05–0.5 mg/ml have been used in our measurements. The lower detection limit for tryptophan by the MCD method is approximately $10^{-5}$ mol/l.

Further applications and a delineation of the scope of this method will be presented subsequently in a full publication.

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**Günter Barth, Ruth Records**
**Edward Bunnenberg, Carl Djerassi***
*Department of Chemistry, Stanford University*
*Stanford, California 94305*
**Wolfgang Voelter**
*Chemisches Institut der Universität Tübingen*
*7400 Tübingen, Germany*
*Received March 1, 1971*

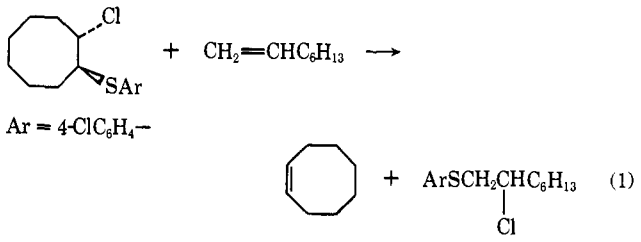
## The Exchange of 4-Chlorobenzenesulfenyl Chloride between Olefins[1]

*Sir:*

We report that the addition product of 4-chlorobenzenesulfenyl chloride with a number of cyclic and acyclic olefins exchanges 4-chlorobenzenesulfenyl chloride with 1-octene when heated in *sym*-tetrachloroethane. Thus, 2-chlorocyclooctyl 4-chlorophenyl sulfide, obtained from the addition of 4-chlorobenzenesulfenyl chloride to *cis*-cyclooctene, gives *cis*-cyclooctene and 2-chlorooctyl 4-chlorophenyl sulfide in quantitative yield after heating for 24 hr in *sym*-tetrachloroethane in the presence of an 8.6 *M* excess of 1-octene (eq 1).

Other chloroalkyl 4-chlorophenyl sulfides that undergo this reaction are listed in Table I along with the time necessary for one-half of the starting material to form the olefin as determined by nmr and vpc analysis of the reaction mixture.

(1) Reactions of Sulfenyl Chlorides and Their Derivatives. IV. Part III: G. H. Schmid, *Can. J. Chem.*, **46**, 3757 (1968).



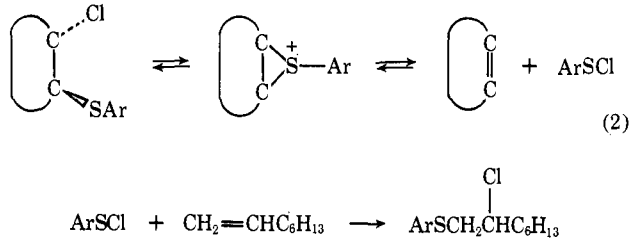

Exchange between 2-chlorooctyl 4-chlorophenyl sulfide and excess cyclooctene (the reverse of eq 1) is not observed.

Table I. Elimination of 4-Chlorobenzenesulfenyl Chloride from Chloroalkyl 4-Chlorophenyl Sulfides, $RSC_6H_4Cl$

| R | Time,[a] hr |
|---|---|
| 2-Chlorocyclononyl | 1.3 |
| 2-Chlorocyclooctyl | 1.5 |
| 2-Chlorocycloheptyl | 40.0 |
| 2-Chlorocyclohexyl | $>2.0 \times 10^3$ |
| 2-Chlorocyclopentyl | 400.0 |
| *erythro*-2-(1-Phenyl-1-chloropropyl) (**1**) | 5.4 |
| *erythro*-3-Chloro-2-butyl | $7.0 \times 10^2$ |
| *erythro*-2-Chloro-1,2-diphenylethyl | 1.8 |
| *threo*-2-Chloro-1,2-diphenylethyl | $>4 \times 10^2$ |

[a] Time necessary for one-half of the starting material to form olefin.

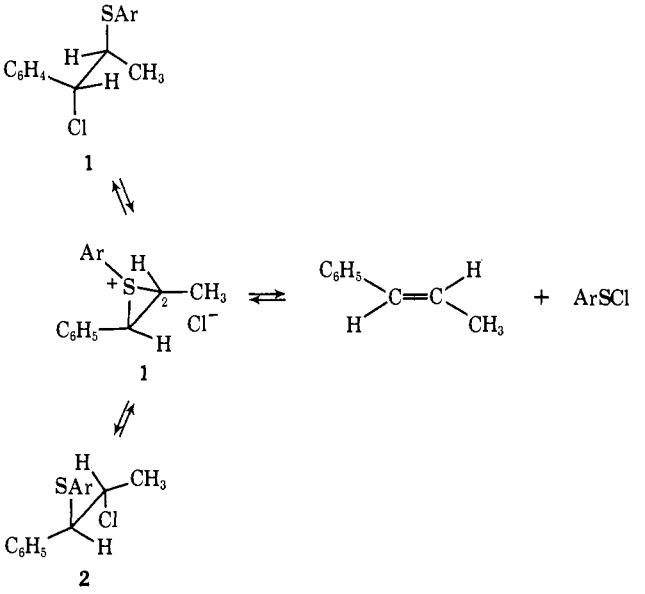
Rearrangements[2] and solvolysis reactions[3] of aryl sulfides have been postulated to occur by means of a mechanism involving a cyclic episulfonium ion which undergoes nucleophilic attack at the carbon atoms. A similar mechanism involving an episulfonium ion can be postulated for this exchange with the additional feature that the nucleophilic attack occurs also at sulfur. The 4-chlorobenzenesulfenyl chloride so formed then adds to the excess 1-octene to complete the reaction (eq 2).




This mechanism is consistent with the work of Helmkamp[4] who found that the reaction of cyclooctene-*S*-methylepisulfonium 2,4,6-trinitrobenzenesulfonate with a variety of nucleophiles occurs more often by attack at sulfur than at carbon. The major difference between our results and those of Helmkamp seems to be in the relative amounts of nucleophilic attack on sulfur compared to carbon. Nucleophilic attack on the episulfonium ion formed by participation of sulfur of the 2-chloroalkyl aryl sulfide occurs predominantly at carbon. This is evident from two results. (1) The solvolysis of 2-chlorocyclooctyl 4-chlorophenyl sulfide in 80% dioxane–water gives as products

(2) G. M. Beverly, D. R. Hogg, and J. H. Smith, *Chem. Ind. (London)*, 1403 (1968); W. A. Thaler, W. H. Mueller, and P. Butler, *J. Amer. Chem. Soc.*, **90**, 2069 (1968).
(3) H. L. Goering and K. L. Howe, *ibid.*, **79**, 6542 (1957).
(4) D. C. Owsley, G. K. Helmkamp, and S. N. Spurlock, *ibid.*, **91**, 3606 (1969).

10% cyclooctene (from sulfur attack) and 90% 2-hydroxycyclooctyl 4-chlorophenyl sulfide (from carbon attack). (2) In addition to exchanging 4-chlorobenzenesulfenyl chloride with 1-octene, *erythro*-1-phenyl-1-chloro-2-propyl 4-chlorophenyl sulfide (**1**) rearranges to *erythro*-1-phenyl-2-chloro-1-propyl 4-chlorophenyl sulfide (**2**) under the same reaction conditions.[5] This rearrangement which involves attack at carbon occurs *faster* than exchange. On the basis of thermodynamic data obtained from a study of the isomerization of **1**




to **2** and initial product data from the addition of 4-chlorobenzenesulfenyl chloride to *trans*-1-phenylpropene[6] we can estimate the relative rates of attack at $C_1$, $C_2$, and S of the intermediate episulfonium ion to be 120:2.4:1.0. Thus attack of carbon is preferred. This is not so surprising since the episulfonium ion formed under these conditions is probably part of an intimate ion pair with the chloride ion which can return to starting material (or its isomer) by carbon attack more easily than form the olefin by attack at sulfur. An alternate mechanism involving attack of 1-octene at the sulfur atom of the episulfonium ion seems unlikely on the basis of Helmkamp's work.

The data in Table I indicate that the structure of the 2-chloroalkyl aryl sulfide has a great effect on the time needed for exchange. These times for exchange represent two different rate processes: the rate of formation of the episulfonium ion and the relative rate of attack of sulfur. While we do not yet have the necessary rate data to quantitatively evaluate these two effects, we can note several factors which seem to be important. The ease of exchange seems to be related to the ease with which the carbon atoms of the episulfonium ion can undergo $sp^2$ hybridization with subsequent formation of the olefin. For the cyclic sulfides, the ease of $sp^2$ hybridization is in the order $9 \approx 8 > 7 \approx 5 \gg 6$ which is close to the order of the ease of exchange.[7] In addition there is a steric hindrance to attack at the backside of the episulfonium ion in the case of the nine-, eight-, and seven-membered rings which is not present in the five- and six-membered rings or the acyclic compounds. Such steric hindrance is believed to be responsible for the much slower nucleophilic ring opening of cyclooctene oxide compared to cyclohexene oxide.[8] The result is to make attack easier at sulfur relative to carbon and consequently exchange is more rapid for the cycloheptyl, cyclooctyl, and cyclononyl sulfides.

The difference in the ease of exchange between the *erythro*- and *threo*-2-chloro-1,2-diphenylethyl 4-chlorophenyl sulfide seems to be a result of eclipsing the two phenyl groups in the case of the threo isomer. Whether this effect is more important in the formation of the intermediate or in the olefin formation is currently under study.

**Acknowledgment.** Financial support from the National Research Council of Canada is gratefully acknowledged.

(5) G. H. Schmid and V. M. Csizmadia, *Chem. Ind. (London)*, 1811 (1968).
(6) G. H. Schmid and V. M. Csizmadia, unpublished results.
(7) J. Sicher, *Progr. Stereochem.*, 3, 224 (1962).
(8) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, 80, 2849 (1958).
(9) Holder of a Province of Ontario Government Fellowship, 1967–1970.

**George H. Schmid,* Patrick H. Fitzgerald**[9]
*Department of Chemistry, University of Toronto*
*Toronto 181, Canada*
*Received February 8, 1971*

## Unusual Metalloporphyrins. VII. A Porphyrin Bridging Two Metal Atoms: μ-[Mesoporphyrin IX dimethyl esterato]bis[tricarbonylrhenium(I)]

*Sir:*

Metalloporphyrins other than ionic species such as those of alkali metals have been found with a single metal atom either in or slightly above the porphyrin plane.[1] Although there has been some interesting speculation on the possibility of metalloporphyrins bonded to two ligands on one side of the porphyrin plane, neither this nor any species containing as many as three "axial" ligands has ever been reported.[1] We would like to report two new metalloporphyrins which seem to illustrate additional categories of porphyrin geometry.

Equimolar quantities of mesoporphyrin IX dimethyl ester and dirhenium decacarbonyl were mixed in decalin and refluxed under argon for 2 hr. The solution was evaporated, dissolved in methanol, and chromatographed on a talc column. A small quantity of red complex, I, followed by a large quantity of brown complex, II, separated as two bands on the column.

μ-[Mesoporphyrin IX dimethyl esterato]bis[tricarbonylrhenium(I)] (I) crystallized from methanol as small dark needles, mp 250–252°, and sublimed under high vacuum at 240°. *Anal.* Calcd for $Re_2C_{42}H_{40}N_4O_{10}$: C, 44.51; H, 3.56; Re, 32.87. Found: C, 44.52; H, 3.99; Re, 32.46. The needles appeared red under a microscope and gave a red solution with visible absorptions in benzene at 519, 480 (shoulder), and 400 nm. The ir spectrum of **I**, both in solution (chloroform) and solid phase (KBr), has strong absorptions at 1900 and 2015 $cm^{-1}$. A deuteriochloroform solution gave a sharp mesoporphyrin spectrum in the pmr, thus

(1) E. B. Fleischer, *Accounts Chem. Res.*, 3, 111 (1970).