THE INFLUENCE OF TEMPERATURE ON THE STEREOCHEMISTRY OF THE ADDITION OF *p*-CHLOROBENZENESULFENYL CHLORIDE TO *cis*- AND *trans*-2-BUTENE

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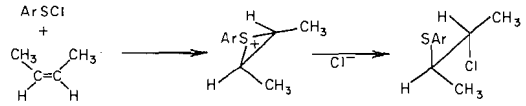
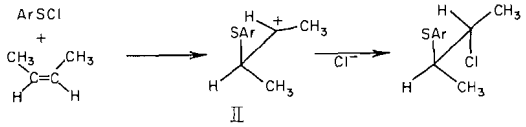
The mechanism of the reaction of an arylsulfenyl chloride with an olefin has been postulated by Kharasch (1) to involve a cyclic sulfonium ion intermediate (I).



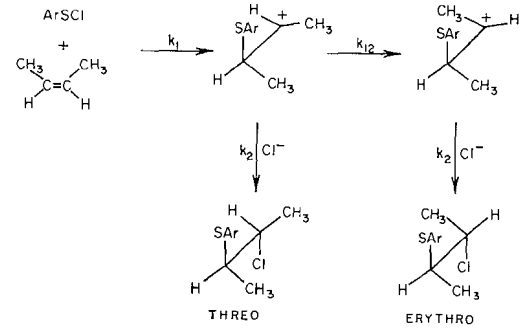
I

This intermediate has been invoked to account for the observed *trans* addition. Evidence that such an intermediate is capable of formation has been obtained by Pettitt and Helmkamp (2) and by Eliel (3). These results do not rule out the formation of an open carbonium ion (II) as an intermediate.



II

trans Addition will be favored because of the steric hindrance of the sulfur group and its substituent. This intermediate would retain its stereochemical integrity if the rate of rotation about the carbon–carbon single bond to form the isomeric carbonium ion is slower than the rate of attack by chloride ion. This mechanism is illustrated in Reaction Scheme 1. The bimolecular step is a reaction between ions of different charge. Such



REACTION SCHEME 1.

reactions have been shown to have extremely fast rates (4), and in addition, energy barriers to rotation in the range of 10 kcal are known (5). Thus, this mechanism cannot be rejected arbitrarily. A method to distinguish between these two mechanisms is to study the effect of temperature on the stereochemistry of the product of the addition of an arylsulfenyl chloride to a *cis* and *trans* olefin. The system chosen for study was the addition of *p*-chlorobenzenesulfenyl chloride to *cis*- and *trans*-2-butene.

[1]*Holder of a Province of Ontario Government Fellowship, 1965–1966.*

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Consider the kinetic scheme for the addition to *cis*-2-butene as illustrated in Reaction Scheme 1. The rates of formation of the threo isomer and the erythro isomer are given by eqs. [1] and [2], respectively.

$$[1] \qquad \frac{\mathrm{d[threo]}}{\mathrm{d}t} = \frac{k_1[cis\ \text{olefin}][\mathrm{ArSCl}]}{1 + (k_{12}/(k_2[\mathrm{Cl}^-]))}$$

$$[2] \qquad \frac{\mathrm{d[erythro]}}{\mathrm{d}t} = \frac{k_1[cis\ \text{olefin}][\mathrm{ArSCl}]}{(k_2[\mathrm{Cl}^-]/k_{12}) + 1}$$

Elimination of time as a variable (6) and integration gives eq. [3].

$$[3] \qquad \frac{[\text{erythro}]}{[\text{threo}]} = \frac{k_{12}}{k_2[\mathrm{Cl}^-]}$$

The relation between the [erythro]/[threo] ratio at any two temperatures is given by eq. [4].

$$[4] \qquad \frac{([\text{erythro}]/[\text{threo}])_{T_1}}{([\text{erythro}]/[\text{threo}])_{T_2}} = L = (k_{12}/k_2)_{T_1}(k_2/k_{12})_{T_2}$$

Replacement of the rate constants by the Arrhenius equation gives eq. [5].

$$[5] \qquad L = \frac{\exp \frac{E_a^{12}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}{\exp \frac{E_a^{2}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

This can be simplified to eq. [6].

$$[6] \qquad \log L = \frac{E_a^{12} - E_a^{2}}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Equation [6] predicts that the ratio L will depend upon the relative activation energies of the two processes and the temperature range chosen to study the product composition. From eq. [6] it is possible to calculate the change in temperature necessary to observe a value of 5 for L if the difference in activation energies is but 2.0 kcal/mole. A temperature range of 150 degrees is predicted. Thus, eq. [6] gives a convenient method of testing the open carbonium ion mechanism. If the energy of activation of rotation is greater than the energy of activation of the bimolecular reaction by at least 2 kcal/mole, a significant change in the [erthyro]/[threo] ratio should be observed as the temperature of the reaction is increased over a range of 150 degrees.

The experimental results of the stereochemistry of the addition of *p*-chlorobenzenesulfenyl chloride to *cis*- and *trans*-2-butene in 1,1,2,2-tetrachloroethane over a temperature range of 180 degrees are given in Table I. The product composition was determined by vapor phase chromatography, which cleanly separated the *dl*-erythro and *dl*-threo isomers. Addition of oxygen, to suppress any free-radical reaction, had no effect upon the product composition. Control experiments showed that a minimum of 0.05% of one isomer could be detected in the presence of the other. The nearly constant 0.5% of threo isomer in the addition to *trans*-2-butene is due to *cis*-2-butene being an impurity in the starting material. The *cis*-2-butene contained less than 0.05% of *trans*-2-butene.

From the data in Table I it is clear that the ratio L given by eq. [4] has a value of 1. Therefore, if eq. [6] is to be consistent with the experimental observations, then $E_a^{12} = E_a^{2} = E$. This means that the difference in rates must be due to the pre-exponential factors.

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TABLE I

Observed temperature effect on product stereochemistry

Temperature (°C)	*cis*-2-Butene		*trans*-2-Butene	
	dl-Erythro	*dl*-Threo	*dl*-Erythro	*dl*-Threo
−34	0.05	99.95	99.44	0.56
0	0.05	99.95	99.55	0.45
25	0.05	99.95	99.49	0.51
50	0.05	99.95	99.46	0.54
75	0.05	99.95	99.56	0.44
100	0.05	99.95	99.49	0.51
146	0.05	99.95	99.54	0.46

Equation [7] is obtained by substitution of the Arrhenius equations for k_{12} and k_2 into eq. [3], and relates the [erythro]/[threo] ratio and the pre-exponential factors.

$$[7] \qquad \frac{[\text{erythro}]}{[\text{threo}]} = \frac{A_{12}\exp(-E/RT)}{A_2\exp(-E/RT)[\text{Cl}^-]} = \frac{A_{12}}{A_2[\text{Cl}^-]}$$

Experimentally, the [erythro]/[threo] ratio is given by eq. [8].

$$[8] \qquad \frac{[\text{erythro}]}{[\text{threo}]} = \frac{0.05}{99.95} = 5 \times 10^{-4} = \frac{A_{12}}{A_2[\text{Cl}^-]}$$

For eq. [8] to be true, the product of the pre-exponential factor A_2 and the chloride ion must be 5×10^4 times the pre-exponential factor A_{12}. This seems to be unlikely. The concentration of chloride ion will be so small (approximately 10^{-8} mole/l) that, even if the pre-exponential factor is among the highest known (10^{19} l moles/s (4)), the product of the two will still be approximately equal to or less than a normal pre-exponential factor for a unimolecular process (10^{10} to 10^{12}/s) involving rotation (7). Thus, for an open carbonium ion mechanism to account for the observed results, it is necessary not only that the activation energies of the rotation and bimolecular steps be identical but also that the pre-exponential factor for the bimolecular step be extremely high.

It seems to be clear that the cyclic sulfonium ion intermediate mechanism originally postulated by Kharasch (1) and supported by the work of Pettitt and Helmkamp (2) and Eliel (3) explains more easily and more satisfactorily not only the *trans* addition but also the absence of a temperature effect upon the stereochemistry of the product.

EXPERIMENTAL

All melting and boiling points are uncorrected. Vapor phase chromatography was performed on a Wilkens Instruments model 705 chromatograph with helium as a carrier gas.

Bis-(4-chlorobenzene)disulfide

In a 2 l Erlenmeyer flask equipped with a magnetic stirrer were placed 1 000 ml of distilled water, 86.7 g (0.60 mole) of *p*-chlorothiophenol, and 24.0 g (0.60 mole) of sodium hydroxide. The crystalline *p*-chlorothiophenol dissolved as a fluffy precipitate of sodium *p*-chlorothiophenoxide was formed. To the mixture was added 450 ml of 3% hydrogen peroxide at such a rate that the temperature of the reaction mixture did not exceed 30 °C. The light-yellow disulfide precipitated as it was formed. After the addition of the hydrogen peroxide, the reaction mixture was stirred overnight at room temperature. The crystals were filtered, and washed with warm tap water and then distilled water until the filtrate was alkaline free. Recrystallization from 95% ethyl alcohol gave a 95% yield of pale-yellow plates, m.p. 73.0–73.5 °C (lit. m.p. 71–71.5 °C (8)).

p-Chlorobenzenesulfenyl Chloride

This compound was prepared by the method of Lawson and Kharasch (9) in 81% yield, b.p. 33–34 °C at 0.22 mm (lit. b.p. 86–90 °C at 5 mm (10)). The purity of the material was determined by the method of Kharasch and Wald (11) and found to be 99.8 ± 1%.

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Reaction of p-Chlorobenzenesulfenyl Chloride with cis- and trans-2-Butene

The reaction was carried out in the dark in a 250 ml, three-necked, round-bottomed flask equipped with a thermometer, a $CaCl_2$ drying tube, a gas inlet tube, and a dry ice – acetone condenser. 1,1,2,2-Tetrachloroethane (40 ml) was placed in the flask and brought to the desired temperature by a liquid ammonia bath, water bath, or oil bath. During this time, dry nitrogen gas was bubbled through the solution. After the desired temperature had been reached, 0.6 g (0.0035 mole) of *p*-chlorobenzenesulfenyl chloride was added to the reaction vessel. As soon as the temperature of the reaction mixture returned to its former value, the butene gas was bubbled in slowly. The reaction was rapid and exothermic. The temperature of the reaction mixture rose by 2–4 °C at the beginning of the reaction. The reaction was judged to be complete upon disappearance of the yellow color of the *p*-chlorobenzenesulfenyl chloride. The time for complete reaction was 1 to 5 min, depending upon the temperature. The flask was removed from the bath and the reaction mixture was analyzed directly by vapor phase chromatography. The *dl*-erythro and *dl*-threo isomers were cleanly separated on a ¼ inch by 13 ft column of 5% Carbowax on Chromosorb G. The yield of product was determined at 25 °C by the same procedure, except that methylene chloride was used as solvent. The solvent was removed under reduced pressure to constant weight. The residue, representing a 99% yield, was shown by vapor phase chromatography to consist of one isomer.

Quantitative Determination of Threo- and Erythro-3-chloro-2-butyl-p-Chlorobenzenesulfide

Two stock solutions were prepared: one containing 60.1 mg of the pure threo isomer in 1.0 ml of 1,1,2,2-tetrachloroethane and another containing 60.6 mg of the pure erythro isomer in 1.0 ml of 1,1,2,2-tetrachloroethane. The pure erythro isomer was prepared from a sample of research grade *trans*-2-butene not previously available to us. By means of microliter syringes, several mixtures of known quantities of each component were prepared. These mixtures were analyzed by vapor phase chromatography under the identical conditions used to analyze the reaction product mixtures. It was found that the limit of detection was 0.05% of one component in the presence of the other.

ACKNOWLEDGMENT

The authors are grateful to the National Research Council of Canada for financial aid.

1. N. KHARASCH and C. M. BUESS. J. Am. Chem. Soc. **71**, 2724 (1949).
2. D. J. PETTITT and G. K. HELMKAMP. J. Org. Chem. **29**, 2702 (1964).
3. E. L. ELIEL, L. A. PILATO, and V. G. BADDING. J. Am. Chem. Soc. **84**, 2377 (1962).
4. A. A. FROST and R. G. PEARSON. Kinetics and mechanism. John Wiley & Sons, Inc., New York. 1953. Chap. 7. p. 113.
5. D. THOMPSON, R. NEWMARK, and C. SEDERHOLM. J. Chem. Phys. **37**, 411 (1962).
6. S. W. BENSON. J. Chem. Phys. **20**, 1605 (1952).
7. A. ALLERHAND and H. S. GUTOWSKY. J. Chem. Phys. **41**, 2115 (1964).
8. A. H. NATHAN and M. T. BOGERT. J. Am. Chem. Soc. **63**, 2363 (1941).
9. D. D. LAWSON and N. KHARASCH. J. Org. Chem. **24**, 858 (1959).
10. M. B. SPARKE, J. L. CAMERON, and N. KHARASCH. J. Am. Chem. Soc. **75**, 4907 (1953).
11. N. KHARASCH and M. M. WALD. Anal. Chem. **27**, 996 (1955).

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