The Addition of 4-Chloro- and 2,4-Dinitrobenzenesulfenyl Chloride to *cis*- and *trans*-1-Phenylpropene[1]

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The *threo-anti*-Markownikoff and *threo*-Markownikoff adducts are the products of addition of 4-chloro- and 2,4-dinitrobenzenesulfenyl chloride to *cis*-1-phenylpropene while only the *erythro* Markownikoff adduct is the product of addition to *trans*-1-phenylpropene. The addition reaction follows second order kinetics, first order in both olefin and arylsulfenyl chloride, with the rate of addition to the *trans*-olefin faster than to the *cis*. These results are consistent with a mechanism involving bridged transition states in both the rate and product determining steps.

Les produits d'addition *thréo-anti*-Markownikoff et *thréo*-Markownikoff sont obtenus par l'action du chlorure de chloro-4 et de dinitro-2,4 benzène sulfényle sur le phényl-1 propène *cis* tandis que la même réaction sur le composé *trans* conduit uniquement au composé d'addition *erythro*-Markownikoff. La réaction d'addition suit des cinétiques d'ordre deux; l'ordre étant de un à la fois pour l'oléfine et pour le chlorure d'arylsulfényle, la vitesse de l'addition sur l'oléfine *trans* est plus rapide que pour le *cis*. Ces résultats sont compatibles avec un mécanisme impliquant des états de transition pontés à la fois pour les étapes déterminantes de la cinétique et du produit.

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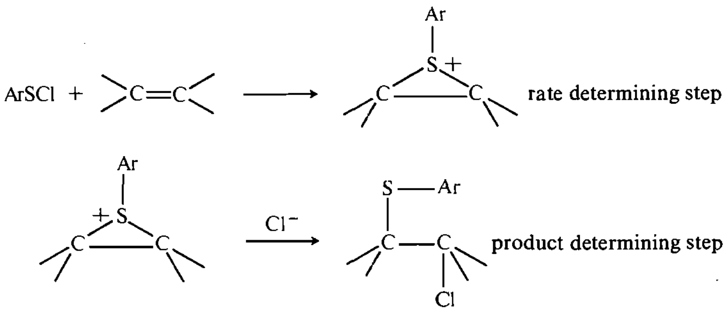
Introduction

The mechanism of the addition of sulfenyl chlorides to olefins has been postulated to involve an episulfonium ion intermediate whose formation is rate determining (Scheme 1) (2, 3). Attack by chloride ion on the intermediate in the product determining step leads to the adduct. In this mechanism both the rate and product determining steps involve bridged transition states. An alternate mechanism which seems to be consistent with the experimental facts involves a bridged transition state in the first step leading to an episulfonium ion intermediate which then opens to a carbonium ion prior to the product determining step (Scheme 2). The *trans* stereospecificity of the reaction is due to the steric hindrance of the adjacent arylthio group which forces the chloride ion to attack from the opposite side. Such a mechanism might be expected in the addition of sulfenyl halides to olefins such as styrene in which the incipient carbonium ion would be of greater stability. We present experimental evidence which has direct bearing upon this question.

Results

The addition of 4-chlorobenzenesulfenyl chloride to *cis*-1-phenylpropene at 25 °C in



SCHEME 1

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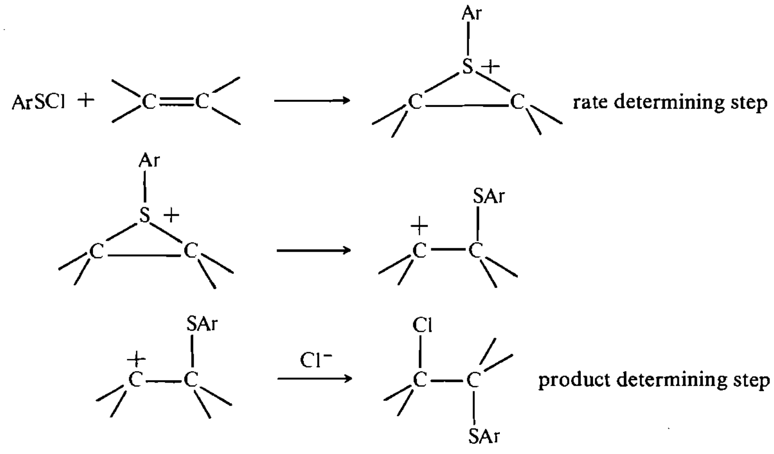
[1] Reactions of Sulfenyl Chlorides and their Derivatives. V. For Part IV see ref. 1*a*. For a preliminary communication, see ref. 1*b*.



Scheme 2

1,1,2,2-tetrachloroethane gives two products, **1** and **2** in 34 and 66% yields respectively, while the addition to *trans*-1-phenylpropene gives initially only compound **3**. After standing for several months at room temperature the formation of a second product, **4**, was observed by n.m.r. No difference in products was observed in the presence of added oxygen or in the presence or absence of light.

It proved possible to obtain a pure sample of each of the four isomers. The pure isomers **2** and **4** were obtained by the slow rearrangement of the corresponding isomers **1** and **3** respectively (4) followed by fractional crystallization. Isomer **1** was obtained by carrying out the addition reaction of the *cis*-olefin in dry formic acid and immediately working-up the product while isomer **3** was the sole product of the addition to the *trans*-olefin at room temperature.

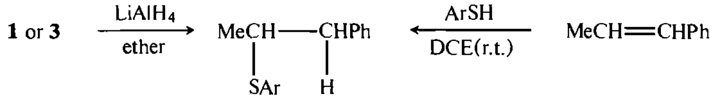
Purification or separation of these adducts by vapor phase chromatography, distillation, or column chromatography proved unsuccessful because of the isomerization tendency of the isomers. The structure and stereochemistry of the four adducts (**1**–**4**) were assigned from their n.m.r. spectra and by chemical means.

The two adducts **1** and **3** were reduced with lithium aluminum hydride to give 1-phenyl-2-(4′-chlorophenylthio)-propane **5** which was prepared by the free radical addition of 4-chlorobenzenethiol to 1-phenylpropene (5) in 1,2-dichloroethane at room temperature (eq. 1).

The two isomers **2** and **4** were treated with boiling potassium *t*-butoxide in *t*-butyl alcohol (6), or 1,5-diazabicyclo[4.3.0]nonene in benzene (7) in the cold (eq. 2). The n.m.r. spectra of the products from both **2** and **4** showed two doublets at δ 2.01 and 1.7 and two quartets at δ 6.38 and 6.16 in CCl_4, indicating that the two olefins, **6** and **7** were formed in the ratio of 4:1. These results are not surprising since elimination of HCl from β-chlorosulfides has been shown to occur non-stereospecifically (8).

On the basis of this evidence compounds **1** and **2** resulting from the addition reaction of the *cis*-olefin were tentatively assigned as the *threo*-Markownikoff (M) and *anti*-Markownikoff (aM) isomers[2] whereas compounds **3** and **4** are

[1]



$$\mathbf{1}\text{ or }\mathbf{3}\ \xrightarrow[\text{ether}]{\text{LiAlH}_4}\ \underset{\text{SAr}}{\text{MeCH}}\text{—}\underset{\text{H}}{\text{CHPh}}\ \xleftarrow[\text{DCE(r.t.)}]{\text{ArSH}}\ \text{MeCH}=\text{CHPh}$$

5

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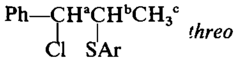
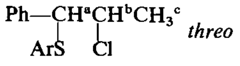
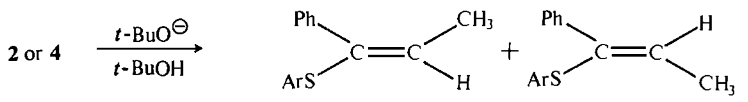
[2] The terms *erythro* and *threo* are not strictly applicable where only one group on adjacent carbon atoms are identical. In this work the name *erythro* is given to the isomer formed by the *trans*-addition to the *trans*-olefin. Also in this work, "Markownikoff" orientation indicates adducts with the chlorine on the benzylic (C_α) carbon while "*anti*-Markownikoff" adducts have the chlorine on the β-carbon.

TABLE 1. The n.m.r. data for the adducts of 4-chlorobenzenesulfenyl chloride and *cis*- and *trans*-1-phenylpropene

Compound	Proton chemical shift*; coupling constants†					m.p. (°C)
	δ_a	J_{ab}	δ_b	J_{bc}	δ_c	
1  $\underset{\mathrm{Cl}}{\mathrm{Ph{-}CH^a}}\underset{\mathrm{SAr}}{\mathrm{CH^b}}\mathrm{CH_3^c}$ *threo*	4.97 (d, 1H)	5.5	3.66 (q, 1H)	7.0	1.23 (d, 3H)	oil
2  $\underset{\mathrm{ArS}}{\mathrm{Ph{-}CH^a}}\underset{\mathrm{Cl}}{\mathrm{CH^b}}\mathrm{CH_3^c}$ *threo*	4.34 (m)	—	4.34 (m)	6.5	1.44 (d, 3H)	59–60
3  $\underset{\mathrm{Cl}}{\mathrm{Ph{-}CH^a}}\underset{\mathrm{SAr}}{\mathrm{CH^b}}\mathrm{CH_3^c}$ *erythro*	4.82 (d, 1H)	7.0	3.49 (q, 1H)	7.0	1.38 (d, 3H)	oil
4  $\underset{\mathrm{ArS}}{\mathrm{Ph{-}CH^a}}\underset{\mathrm{Cl}}{\mathrm{CH^b}}\mathrm{CH_3^c}$ *erythro*	4.14 (d)	7.0	4.32 (q)	6.5	1.54 (d, 3H)	65–67

*In p.p.m. from internal TMS in CCl_4; d, doublet; q, "quintet"; m, multiplet.
†J in Hz.

[2]



6 **7**

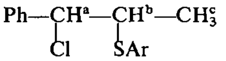
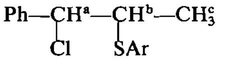
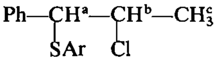
the *erythro*-Markownikoff and *anti*-Markownikoff isomers respectively.

The n.m.r. spectra of the isomers, given in Table 1, are in accord with these structural assignments. From an examination of the n.m.r. spectra of a series of racemic *erythro*- and *threo*-isomers of 1,2-disubstituted 1-arylpropanes, it has been found (9) that the methyl protons of the *erythro*-isomer always appear at lower field than those of the *threo*-isomer. On this basis compounds **1** and **3** resulting from *trans*-Markownikoff addition to *cis*- and *trans*-1-phenylpropene are the *threo*- and *erythro*-isomers respectively whereas compounds **2** and **4** are the *threo*- and *erythro*-isomers respectively of the *anti*-Markownikoff addition. In the two Markownikoff adducts **1** and **3** the peaks of the vicinal hydrogens are well separated and they can easily be identified. The benzylic hydrogen on the carbon bearing the chloride appears at lower field as a doublet, while the hydrogen on the β-carbon, 1 p.p.m. upfield, appears as a "quintet".

The crystalline *anti*-Markownikoff adducts have more complex spectra. The vicinal hydrogens overlap and only the spectrum of the *erythro*-*anti*-Markownikoff product can be resolved into a doublet and "quintet" by the HA-100 n.m.r. spectrometer. This complexity is due to the fact that in the *anti*-Markownikoff adducts the chlorine is now attached to the carbon bearing the methyl group and consequently both the methyl doublet and hydrogen "quintet" are shifted to lower field, while the benzylic hydrogen doublet shifts to higher field because of the presence of the less electronegative sulfur.

The addition of 2,4-dinitrobenzenesulfenyl chloride to *trans*-1-phenylpropene in 1,2-dichloroethane at 25° yields a single yellow crystalline product **8**. The addition to the *cis*-olefin results in a mixture of two products **9** and **10** in a ratio of 60:40, which can be separated by fractional crystallization. The products are stable and they do not rearrange at room temperature. The stereochemistry of the three adducts **8**, **9**, and **10** was assigned from their n.m.r. spectra, based on the knowledge gained in the addition of 4-chlorobenzenesulfenyl chloride. It is thus concluded that the *trans*-olefin gives only Markownikoff oriented addition product **8** while the *cis*-olefin gives both the Markownikoff **9** and the *anti*-Markownikoff addition product **10**. The n.m.r. spectra of the

TABLE 2. The n.m.r. data* for the adducts of 2,4-dinitrobenzenesulfenyl chloride to *cis*- and *trans*-1-phenylpropene

Compound†	H_a	J_{ab}	H_b	J_{bc}	H_c	m.p. (°C)
 $\mathrm{Ph{-}\underset{Cl}{CH^a}{-}\underset{SAr}{CH^b}{-}CH_3^c}$ *erythro*-M	5.06(d)‡	7.0	3.99(q)‡	7.0	1.66(d)	92–93
 $\mathrm{Ph{-}\underset{Cl}{CH^a}{-}\underset{SAr}{CH^b}{-}CH_3^c}$ *threo*-M	5.12(d)	6.0	4.07(q)	7.0	1.45(d)	75–76
 $\mathrm{Ph{-}\underset{SAr}{CH^a}{-}\underset{Cl}{CH^b}{-}CH_3^c}$ *threo*-aM	4.70(d)	6.0	4.47(q)	6.5	1.56(d)	131–132

*δ (p.p.m.) from TMS, 4.2% (g/v) in CCl_4; *J* in Hz.
†Ar, 2,4-dinitrophenyl.
‡d, doublet; q, "quintet".

TABLE 3. Specific rate constant for the addition of 4-chlorobenzenesulfenyl chloride to *cis*-1-phenylpropene in tetrachloroethane at 25°

$[ArSCl]_0 \times 10^3$ (mol/l)	$[cis\text{-olefin}]_0 \times 10^2$ (mol/l)	k $(M^{-1}\,s^{-1})$	No. of runs
1.017	1.250	42.5±0.2	4
8.136	1.250	43.0±0.3	1
1.017	2.500	43.3±0.3	3
10.170	2.500	43.4±0.6	4
10.170	3.526	40.1±0.2	2
10.170	6.632	39.2±0.3	2
10.170	2.724	45.9±0.3	2
	Weighted mean (10)	43.0±0.2	

TABLE 4. Specific rate constant for the addition of 4-chlorobenzenesulfenyl chloride to *trans*-1-phenylpropene in tetrachloroethane at 25°

$[ArSCl]_0 \times 10^3$ (mol/l)	$[trans\text{-olefin}]_0 \times 10^2$ (mol/l)	k $(M^{-1}\,s^{-1})$	No. of runs
10.170	3.870	125.6±0.8	2
10.170	2.322	125.5±0.6	2
10.170	7.544	109.5±0.7	2
7.670	5.066	112.1±0.8	2
7.798	2.724	113.4±0.4	3
1.017	7.544	115.5±0.8	2
	Weighted mean (10)	118.3±0.7	

pure adducts are very straightforward and easy to analyze. Table 2 summarizes the n.m.r. characteristics of the three adducts.

The rate of the addition of 4-chlorobenzenesulfenyl chloride to *cis*- and *trans*-1-phenylpropene in 1,1,2,2-tetrachloroethane at 25° was followed by the stopped-flow technique using a Durrum–Gibson stopped-flow spectrophotometer. The rate of disappearance of 4-chlorobenzenesulfenyl chloride was followed by measuring the decrease in its absorption at 392.5 nm. The addition was found to exhibit normal second order kinetics, first order in olefin and first order in sulfenyl chloride, to 80% completion of the reaction. The results are given in Tables 3 and 4.

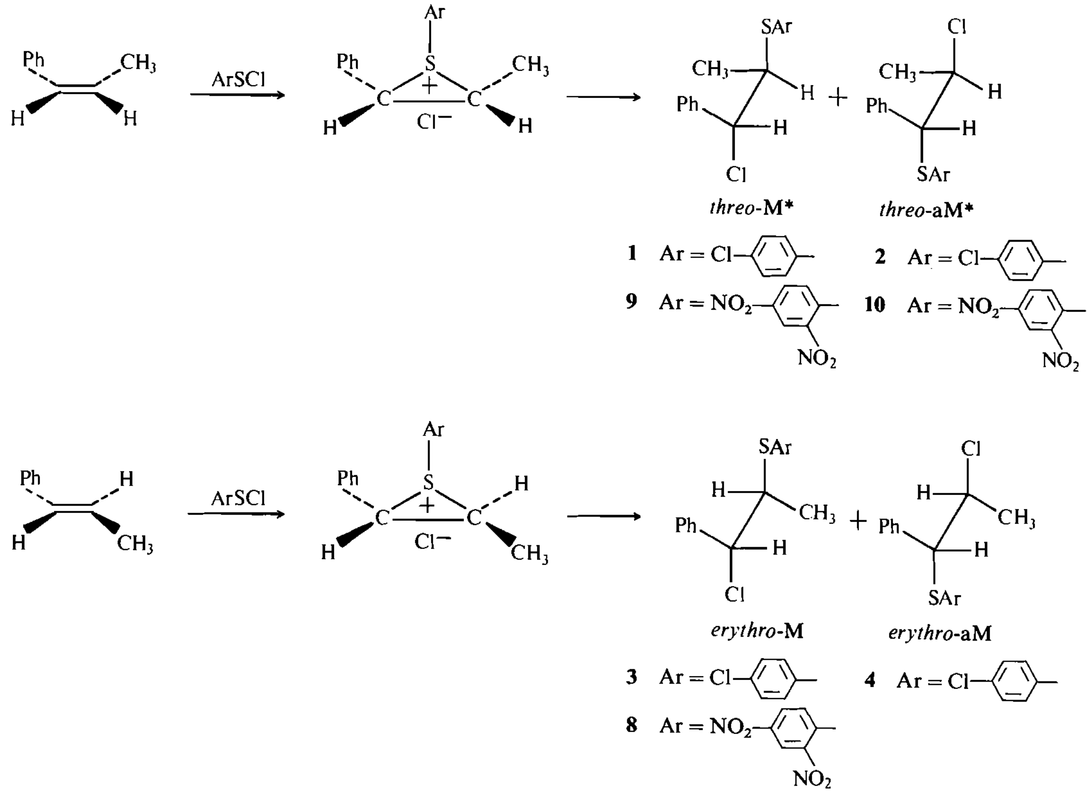
The rate of the addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*- and *trans*-1-phenylpropene in 1,1,2,2-tetrachloroethane at 30° was followed by the usual titration technique (14). Again the reaction was found to exhibit normal second order kinetics; first order in olefin and first order in sulfenyl chloride. The results are given in Table 5.

TABLE 5. Specific rate constants for the addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*- and *trans*-1-phenylpropene in tetrachloroethane at 30°

Olefin	$[\text{olefin}]_0 \times 10^2$ (mol/l)	$[ArSCl]_0 \times 10^3$ (mol/l)	$k \times 10^4$ $(M^{-1}\,s^{-1})$
trans	6.250	8.468	5.98± .02
cis	5.465	11.40	2.80± .04
cis	7.292	12.70	2.80± .04
		Average	2.84± .05

Discussion

From the results presented in this paper, it is clear that the addition of 4-chloro- and 2,4-dinitrobenzenesulfenyl chloride to *cis*- and *trans*-1-phenylpropene is stereospecifically *trans*



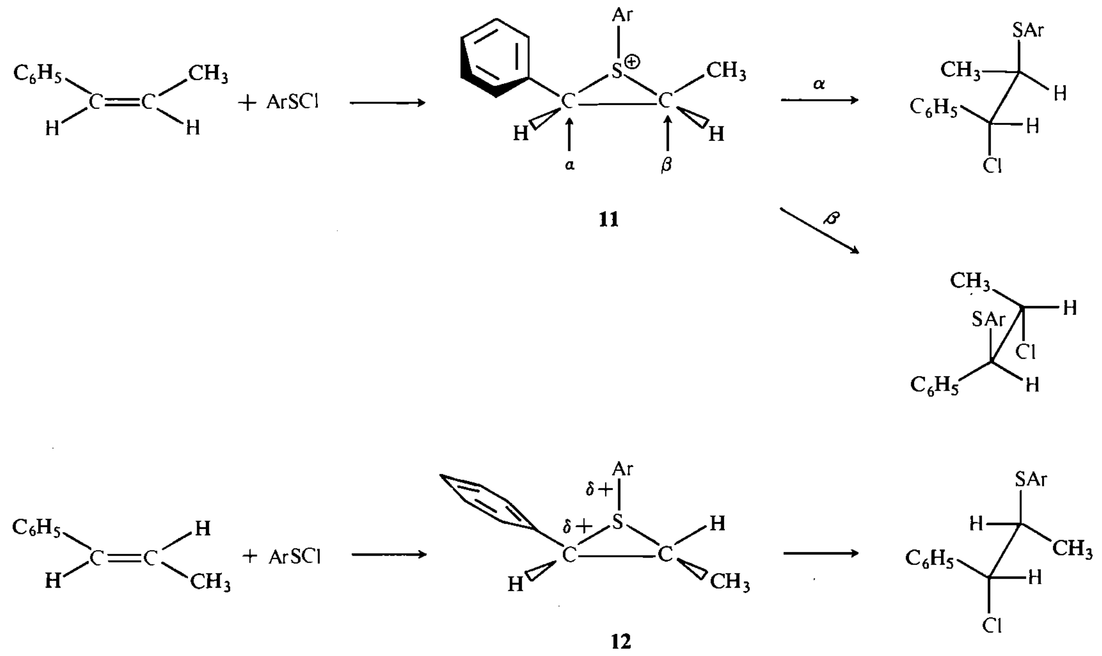
*M = Markownikoff; aM = *anti*-Markownikoff

SCHEME 3

within the limits of our n.m.r. analysis. This result as well as the formation of the *anti*-Markownikoff product in the addition to the *cis*-olefin can best be explained by a mechanism involving transition states that resemble the intermediate episulfonium ion in both the rate and product determining steps. This mechanism is illustrated in Scheme 3. These results can be contrasted with other ionic additions to *cis*- and *trans*-1-phenylpropene. The additions of bromine (11) and chlorine (6) are nonstereospecific and are postulated to involve an open benzylic carbonium ion – ion pair mechanism indicating that the benzyl carbonium ion is more stable than the bridged "halonium" ion. Our results show that the episulfonium ion is more stable than a benzylic carbonium ion as an intermediate in the addition of arylsulfenyl chlorides to *cis*- and *trans*-1-phenylpropene. Such a result is consistent with the relative abilities of sulfur, chlorine, and bromine to act as a neighboring group.

It is interesting that the products are analogous for the addition of either 4-chloro or 2,4-dinitrobenzenesulfenyl chloride. Thus the ortho nitro group does not seem to be involved in the product determining step in contrast to its apparent involvement in other reactions (12).

An interesting finding of the work is that the addition to the *trans*-olefin initially yields only the *erythro*-Markownikoff product while the *cis*-isomer yields both the *threo*-Markownikoff and *anti*-Markownikoff products. These results can be accounted for on the basis of the difference in steric crowding in the two intermediate episulfonium ions (see Scheme 4). The steric crowding is more severe in the case of the episulfonium ion intermediate formed by the addition to the *cis* than the *trans* olefin. As a result, these two intermediates have a small but significant difference. The steric crowding in the *cis* episulfonium ion prevents the phenyl ring from assuming a position where it can assist in stabilizing the positive charge on the adjacent



SCHEME 4

benzylic carbon. As a result, it has a more symmetrical electronic structure **11** than the one from the *trans*-olefin **12**. This difference in the structure of the two episulfonium ions is carried into the product determining transition states. Thus the two transition states for attack of chloride ion at the α and β carbons of **11** are of comparable energy resulting in the formation of products with both Markownikoff and *anti*-Markownikoff orientation. In the case of chloride attack on intermediate **12**, the transition state for attack at the benzylic carbon is of lower energy than the one for attack at the β carbon resulting in the formation of only the Markownikoff product.

If steric crowding in the intermediate episulfonium ions affects the relative energy levels of the product determining transition states, such steric crowding should also be present in the rate determining step leading to these intermediates. The kinetic data are consistent with this idea. Thus in the addition of both 4-chloro- and 2,4-dinitrobenzenesulfenyl chloride to 1-phenylpropene, the *trans*-isomer reacts faster than the *cis* even though the ground state energy of the *trans*-isomer is the lower. This is in contrast to the results of chlorination where *cis*-1-phenylpropene reacts faster than the *trans*-isomer (17). The energy of the rate determining transition state for the addition of arylsulfenyl chloride to the *cis*-isomer must therefore be higher than that of the *trans*-isomer. This is consistent with the formation of a bridged rate determining transition state which shows increased steric interaction over that in the ground state. The difference in the energies between the two transition states must be greater than the 2.8 kcal/mol difference in the starting olefins.

Experimental

All melting points and boiling points are uncorrected. Microanalyses were carried out by A. B. Gygli Microanalysis Laboratory, Toronto.

cis- and trans-1-Phenylpropene

These compounds were obtained commercially from Columbia or Aldrich Chemical Company and their purity was verified by v.p.c. and n.m.r. (b.p. *cis* 160 °C/760 mm, *trans* 98 °C/84 mm).

Bis(2,4-Dinitrophenyl)disulfide

This disulfide was obtained commercially from Eastman Organic Chemicals and used without purification (m.p. 240–280 °C (dec.)).

Bis(4-chlorobenzene)disulfide

In a 2 l Erlenmeyer flask equipped with a magnetic stirrer were placed 1000 ml of distilled water, 86.7 g (0.60 mol) of *p*-chlorothiophenol, and 24.0 g (0.60 mol) 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. 73.0–77.5 °C (lit. (2) m.p. 71–71.5 °C).

p-Chlorobenzenesulfenyl Chloride

This compound was prepared by the method of Lawson and Kharasch (13) in 81% yield, b.p. 33–34 °C at 0.22 mm (lit. (13) b.p. 86–90 °C at 5 mm). The purity of the material was determined by the method of Kharasch and Wald (14) and found to be 99.8 ± 1%.

2,4-Dinitrobenzenesulfenyl Chloride

This compound was prepared by the method of Kharasch *et al.* (15) in 85% yield, m.p. 97–98 °C (lit. (15) m.p. 95–95.5 °C).

1,1,2,2-Tetrachloroethane

This compound was purified by washing with concentrated H_2SO_4 until the acid wash remained colorless. The solvent was then washed with water until neutral, dried over K_2CO_3, then distilled from K_2CO_3 through a Vigreux column, b.p. 146° (lit. (16) b.p. 146°).

The Reaction of p-Chlorobenzenesulfenyl Chloride with cis- and trans-1-Phenylpropene

General Procedure

A solution of *p*-chlorobenzenesulfenyl chloride (1.18 g, 0.01 mol) in 20 ml 1,1,2,2-tetrachloroethane (TCE) was added dropwise to a solution containing 1.79 g (0.01 mol) of either *cis*- or *trans*-1-phenylpropene in 20 ml of TCE at room temperature. The reaction mixture was stirred and it immediately became opaque, then a very fine floating precipitate separated. The reaction mixture was allowed to stand in the dark and the precipitate disappeared. After the solvent was evaporated in a stream of nitrogen gas, the residual oil which corresponded to a quantitative yield was analyzed by n.m.r.

I. Preparation of the Pure anti-Markownikoff threo-Adduct (2)

The general procedure given above was followed except that 1,2-dichloroethane was used as solvent and the reaction mixture was refluxed until the n.m.r. spectrum indicated that the equilibrium product ratio was reached. Then the solvent was evaporated and the residual oil was dissolved in *n*-pentane and was allowed to stand in the refrigerator until crystals formed. The solvent was decanted quickly from the crystals, which were then recrystallized repeatedly from *n*-pentane until its n.m.r. indicated that the pure *anti*-Markownikoff product had been obtained. The colorless solid melted at 59–60 °C.

Anal. Calcd. for $C_{15}H_{14}Cl_2S$: C, 60.61; H, 4.74; Cl, 23.85; S, 10.68. Found: C, 60.67; H, 4.68; Cl, 23.88; S, 10.76.

II. Preparation of the Pure threo-Markownikoff Adduct (1)

The *threo*-Markownikoff addition product was prepared by carrying out the addition in dry formic acid, shaking it, then pouring it very quickly into ice water and extracting with chloroform. The chloroform extract was washed with 5% ice-cold $NaHCO_3$ and then dried over $MgSO_4$. After evaporation of the solvent the oily product was found, by n.m.r., to be the Markownikoff product contaminated by disulfide. No purification method was found because of the isomerization tendency of the Markownikoff adduct to the *anti*-Markownikoff adduct. However, the oil was stable for months at −20 °C.

III. Preparation of the Pure erythro-Markownikoff Adduct (3)

The general procedure was followed except that the *trans*-olefin was used and in this case only the *erythro*-Markownikoff addition product was obtained. The n.m.r. was taken directly on the oil because no purification method has been found which did not also cause isomerization.

IV. Preparation of the Pure anti-Markownikoff erythro-Adduct (4)

The *erythro-anti*-Markownikoff product was obtained in low yield by a method analogous to that of the *threo*-isomer except that the *trans*-olefin was used, m.p. 67–68 °C.

Anal. Calcd. for $C_{15}H_{14}Cl_2S$: C, 60.61; H, 4.74; Cl, 23.85; S, 10.78. Found: C, 60.59; H, 4.65; Cl, 23.95; S, 10.69.

Reduction of the threo- and erythro-Markownikoff Addition Products Obtained from cis- and trans-1-Phenylpropene and p-Chlorobenzenesulfenyl Chloride

The addition product, 5.94 g (0.02 mol), was dissolved in 100 ml of dry ether and a solution of $LiAlH_4$ (0.60 g, 0.04 mol) in 100 ml ether was added in small portions while the reaction mixture was stirred with a magnetic stirrer in a three-necked round-bottomed flask, equipped with a reflux condenser. The reaction mixture was left stirring for 1 h at room temperature. The excess $LiAlH_4$ was destroyed by adding ethyl acetate dropwise, followed by aqueous HCl until a clear liquid separated which was decanted. Ether was added, the mixture stirred, and the ether decanted again. The combined ethereal solution was washed three times with aqueous Na_2CO_3 (because of the very strong mercaptan smell it was also washed twice with dilute NaOH solution), then with distilled water, and dried over anhydrous Na_2SO_4. Concentration on the rotary evaporator gave 4.86 g yellowish oil (yield 83%). Chromatography on a 4 × 48 cm silica gel (28–200 mesh) column using petroleum ether, CCl_4, and $CHCl_3$, followed by concentration of appropriate fractions, gave 3.17 (65% yield) of a pale yellow oil.

Anal. Calcd. for $C_{15}H_{15}ClS$: C, 68.55; H, 5.75; Cl, 13.49; S, 12.20. Found: C, 68.26; H, 5.67; Cl, 14.06; S, 12.23.

Addition of p-Chlorothiophenol to trans-1-Phenylpropene

The addition reaction was carried out by the method of Posner (5) affording a yellowish oil which was purified by column chromatography. The purified adduct was characterized by n.m.r. which was identical to that of the $LiAlH_4$ reduced adduct.

Dehydrochlorination of the Markownikoff and anti-Markownikoff Addition Products Obtained from p-Chlorobenzenesulfenyl Chloride and cis- and trans-1-Phenylpropene

Two methods were used: (1) When the reaction was carried out by the technique described by Fahey and Schubert (6) using potassium *t*-butoxide in *t*-butyl alcohol, all four isomers appeared to give the same olefinic product mixture in a ratio of 80:20. (2) When the method of Eiter and Oedinger (7) was used with 1,5-diazabicyclo[4.3.0]nonene

(DBN) in benzene, the Markownikoff adducts did not react, while the *anti*-Markownikoff adducts gave the same olefinic product mixture as with Fahey's method.

The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with cis- and trans-1-Phenylpropene

In general the addition reaction was carried out as previously described in dry 1,2-dichloroethane and the reaction mixture was analyzed by n.m.r.

I. Preparation of the Pure erythro-Markownikoff Adduct (8)

To a solution of 2.35 g (0.01 mol) of 2,4-dinitrobenzenesulfenyl chloride in 20 ml 1,2-dichloroethane was added slowly 1.18 g (0.01 mol) of *trans*-1-phenylpropene in 20 ml 1,2-dichloroethane while dry nitrogen gas was bubbled through the reaction mixture. The flask was stoppered and was allowed to stand at room temperature in the dark. The end of the reaction was confirmed by the disappearance of the olefinic methyl peak in the n.m.r. spectrum (~16 h).

The solvent from the yellow reaction mixture was removed on a rotary evaporator and the crude oily residue was analyzed by n.m.r. which indicated a single product. The crude product was recrystallized repeatedly from carbon tetrachloride, m.p. 92–93 °C.

Anal. Calcd. for $C_{15}H_{13}O_4N_2ClS$: C, 51.07; H, 3.71; N, 7.94; Cl, 10.05; S, 9.09. Found: C, 51.06; H, 3.70; N, 7.87; Cl, 10.23; S, 9.14.

II. Preparation of the Pure threo-Markownikoff (9) and threo-anti-Markownikoff (10) Adduct

The addition reaction was carried out by the same technique described in section I. The n.m.r. analysis of the crude reaction product indicated the presence of two addition products. The separation of the two adducts by fractional crystallization proved to be the only method.

The crude reaction mixture was dissolved in a mixture of chloroform and *n*-hexane (9:1) at room temperature and the solution was allowed to stand in the refrigerator until a solid separated. After filtration both the solid and the filtrate were analyzed by n.m.r. The solid, which was enriched in the *threo-anti*-Markownikoff adduct, was dissolved again in a mixture of chloroform and *n*-hexane (9:1) and was kept in the refrigerator for crystallization. The filtrate, which was enriched in the *threo*-Markownikoff adduct, was concentrated to a small volume by means of the rotary evaporator and returned to the refrigerator. The process was repeated until n.m.r. analysis indicated that the pure addition products were obtained.

Kinetic Procedure

(a) Stopped-Flow

All kinetic runs were carried out on a Durrum-Gibson stopped-flow spectrophotometer. Prior to any set of kinetic runs the instrument was allowed to stabilize for at least 2 h. A constant temperature bath was maintained at 25.00 ± 0.03°. The instrument was checked out and calibrated prior to each set of runs. Zero and 100% transmittance lines were determined by running pure solvent *vs.* the olefin solution. The time base was accurate to ±1–2% on any time scale. Kinetic runs with each olefin were carried out until a reproducible trace was stored on the oscilloscope. An infinity line was added after an appropriate time lapse. The single run was then recorded on type 107 B & W Polaroid film. Measurements from the film were treated in the usual manner (10).

(b) Titration

An adaptation of the method of Kharasch and Wald (14) was used to follow the decrease in concentration of the sulfenyl chloride. Rate constants were calculated from the slope of the straight line obtained by a least square fit to the second order rate equation.

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