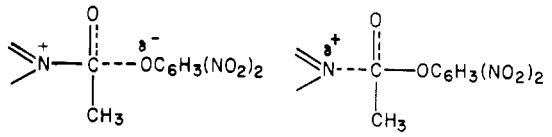
phenyl methyl carbonates), and this is far beyond the $pK_a$ range covered by substituted pyridines.

The Brønsted slope obtained for MPC (Figure 1) has a value of 1.3, which is higher than the values generally obtained for the corresponding slopes in aminolysis reactions of phenyl acetate[1] ($\beta$ = 1.0) and other carbonyl compounds of similar reactivity[1,4,5] ($\beta$ = 0.9–1.0). The higher $\beta$ value for MPC than for 2,4-dinitrophenyl methyl carbonate in the low $pK_a$ region[6] ($\beta_2$ = 0.9) in their reactions with substituted pyridines is consistent with a small increase in selectivity with decreasing reactivity over a wide range of reaction rates, according to Hammond[15] and other authors.[16]

The curved Brønsted plot of Figure 1 could also be described by assuming a one-step reaction and by using a treatment based on a change in transition-state geometry (a Hammond postulate[15] effect). This treatment has also been applied to the pyridinolysis reactions of methyl chloroformate,[17] but, as in the present case, the Brønsted curvature predicted is almost unnoticeable over the $pK_a$ range covered by the substituted pyridines.

The more negative value of $\Delta S^{\ddagger}$ obtained for the reaction of DNPA with 3-chloropyridine compared to that with 4-(dimethylamino)pyridine is in accord with the transition-state structures expected for rate-determining phenolate expulsion (I) and rate-determining pyridine attack (II), respectively. A change from rate-determining addition to rate-determining elimination has been reported to be accompanied by a large decrease of $\Delta S^{\ddagger}$ in nucleophilic vinylic substitution reactions.[18]



I II

According to what has been discussed here and elsewhere,[4,14] the relative leaving abilities of oxygen and nitrogen bases from a tetrahedral intermediate depend not only on their nature but also on the nature of both the nonleaving group and other groups in the electrophilic reactant. We plan further work to study the influence of the group that does not leave on the relative leaving abilities of pyridines and phenolates for given systems.

**Acknowledgment.** The authors wish to thank the Dirección de Investigación de la Universidad Católica de Chile for financial support.

**Registry No.** 2,4-Dinitrophenyl acetate, 4232-27-3; 3-cyanopyridine, 100-54-9; 4-cyanopyridine, 100-48-1; 3-chloropyridine, 626-60-8; nicotinamide, 98-92-0; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 4-aminopyridine, 504-24-5; 4-(dimethylamino)pyridine, 1122-58-3; phosphate dianion, 14265-44-2; methyl phenyl carbonate, 13509-27-8; water, 7732-18-5; hydroxide ion, 14280-30-9.

(15) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
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(19) E. A. Castro and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 658 (1974).

# Rates and Products of Addition of 4-Chlorobenzenesulfenyl Chloride to a Series of Methyl-Substituted 1,3-Butadienes[1]

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The rate and products of addition of 4-chlorobenzenesulfenyl chloride to 1,3-butadiene and 11 of its mono- and dimethyl derivatives have been determined in 1,1,2,2-tetrachloroethane at 25 °C. Substituting one of the hydrogens on 1,3-butadiene by a methyl group increases the rate of addition. The increase varies between 1.4 and 8.2 and depends upon the location of the methyl group relative to the double bond at which addition occurs. A slight preference for addition to the least substituted double bond is found. In general 1,2-adducts are formed in an anti-stereospecific manner. Upon standing the initial products isomerize to the 1,4-adducts in all cases except the adduct of addition to 1,3-butadiene. The results are consistent with a mechanism involving thiiranium ion like rate- and product-determining transition states.

Electrophilic additions to conjugated dienes are known to form products of 1,2 and 1,4 addition.[3] The proportions of these products and their stereochemistry have been determined for the reactions of numerous electrophiles with a number of different dienes. To our knowledge, however, no investigations have examined the effect of the structure of the conjugated diene upon the rate of electrophilic addition. We present some results on this neglected aspect of electrophilic additions to conjugated dienes.

(1) Reactions of Sulfenyl Chlorides and Their Derivatives. 20. For part 19, see G. H. Schmid, D. G. Garratt, and S. Yeroushalmi, *J. Org. Chem.*, **43**, 3764 (1978).
(2) Division of Chemistry, National Research Council, Ottawa, Ontario, K1A 0R6.
(3) (a) G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *J. Org. Chem.*, **38**, 4109 (1973); (b) V. L. Heasley, C. N. Griffith, and G. E. Heasley, *ibid.*, **40**, 1358 (1975); (c) G. E. Heasley, D. C. Hayse, G. R. McClung, D. K. Strickland, V. L. Heasley, P. D. Davis, D. M. Ingle, K. R. Rold, and T. S. Ungermann, *ibid.*, **41**, 334 (1976); (d) G. E. Heasley, V. M. McCully, R. T. Wiegmann, V. L. Heasley, and R. A. Skidgel, *ibid.*, **41**, 644 (1976); (e) D. F. Shellhamer, V. L. Heasley, J. E. Foster, J. K. Luttrull, and G. E. Heasley, *ibid.*, **43**, 2652 (1978); (f) G. E. Heasley, J. M. Bundy, V. L. Heasley, S. Arnold, A. Gipe, D. McKee, R. Orr, S. L. Rodgers, and D. F. Shellhamer, *ibid.*, **43**, 2793 (1978).

0022-3263/80/1945-0910$01.00/0 

Table I. Rates of Addition of 4-Chlorobenzenesulfenyl Chloride to 1,3-Butadiene and a Series of Its Methyl-Substituted Derivatives in 1,1,2,2-Tetrachloroethane at 25 °C

| diene | compd no. | $k_2$, $M^{-1}$ $s^{-1}$ | $k_{rel}$ |
|---|---|---|---|
| $CH_2=CH-CH=CH_2$ | 1 | 27.8 ± 0.1 | 1 |
| $CH_2=C(CH_3)CH=CH_2$ | 2 | 125 ± 1 | 4.5 |
| $CH_2=C(CH_3)C(CH_3)=CH_2$ | 3 | 162 ± 1 | 5.8 |
| (Z)-$CH_2=CH-CH=CHCH_3$ | 4 | 165 ± 1 | 5.9 |
| (E)-$CH_2=CH-CH=CHCH_3$ | 5 | 244 ± 1 | 8.8 |
| $CH_2=CH-CH=C(CH_3)_2$ | 6 | 1114 ± 5 | 40 |
| (Z)-$CH_2=CH-C(CH_3)=CHCH_3$ | 7 | 276 ± 1 | 10 |
| (E)-$CH_2=CH-C(CH_3)=CHCH_3$ | 8 | 475 ± 2 | 17 |
| (Z,Z)-$CH_3CH=CH-CH=CHCH_3$ | 9 | 671 ± 2 | 24 |
| (E,Z)-$CH_3CH=CH-CH=CHCH_3$ | 10 | 742 ± 2 | 26 |
| (E,E)-$CH_3CH=CH-CH=CHCH_3$ | 11 | 768 ± 3 | 27 |
| (E)-$CH_2=C(CH_3)-CH=CHCH_3$ | 12 | 1260 ± 10 | 45 |

## Results

The rates of addition of 4-chlorobenzenesulfenyl chloride to 1,3-butadiene (1) and 11 of its methyl-substituted derivatives (2–12) (for structures see Table I) were measured in 1,1,2,2-tetrachloroethane at 25 °C by means of the stopped-flow technique using a Durrum-Gibson stopped-flow spectrophotometer. All the rates were measured under pseudo-first-order conditions. The data of all runs gave linear first-order plots. The second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the diene concentration. The rate data are given in Table I.

Product stereochemistry and regiochemistry were established by $^1H$ and $^{13}C$ magnetic resonance by use of data previously obtained from the adducts of addition of arenesulfenyl and areneselenenyl chloride to simple alkenes.[4] Using these data, we have made the proton assignments given in Table II for the 1,2-adducts formed under kinetic control. In general, it has been found that (i) the protons of a methyl group $\beta$ to sulfur ($CH_3CHS$) appear at or near $\delta$ 1.4 while the corresponding protons $\beta$ to chlorine ($CH_3CHCl$) appear at or near $\delta$ 1.7; (ii) the protons of a vinyl methyl group ($CH_3CH=$) appear near $\delta$ 1.65; and (iii) a methine proton on a carbon bearing an arylthio group (CHSAr) appears in the region $\delta$ 3.2–3.6, upfield from the corresponding proton adjacent to chlorine. These assignments are corroborated by the $^{13}C$ NMR data in Table III.

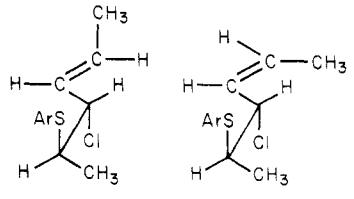
From the $^{13}C$ NMR spectra of the adducts formed by addition to (E,E)-, (Z,E)-, and (Z,Z)-2,4-hexadiene, it is possible to establish their stereochemistry. The two $\alpha$ carbons of compounds of type **13** have been found to be

$$\overset{\alpha}{R}CH_2CH(Cl)CH(SAr)\overset{\alpha}{C}H_2R$$

**13**

considerably deshielded in the erythro configuration relative to the same two carbons in the threo configuration. This seems to be a general relationship as illustrated by the data in Table IV.[5] From this relationship, it is clear that the pairs of adducts **14**:**15** and **16**:**17** are erythro and threo isomers. Thus the products are formed by anti-stereospecific addition.

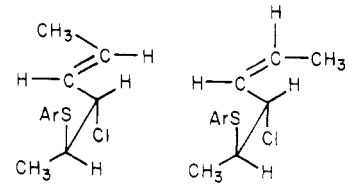
The $^{13}C$ NMR data also allow us to establish the configuration of the unreacted double bond. The $^{13}C$ NMR




**14**




**15**




**16**




**17**

chemical shifts of carbons attached to a carbon–carbon double bond appear at higher field for the Z than for the E isomer.[6] The olefinic methyl group of the adduct **17**, formed by addition to (Z,Z)-2,4-hexadiene, is shielded relative to the olefinic methyl group of the adduct **14** formed by addition to (E,E)-2,4-hexadiene. Thus the addition occurs with retention of configuration of the unreacted double bond.

The products of addition are given in Table V. The major products under conditions of kinetic control are always the 1,2-adducts. In most cases, they isomerize to the 1,4-adducts whose $^{13}C$ NMR spectra (where available) are give in Table VI. The rate at which this occurs varies from a few minutes to several days. In many cases, the initial product composition contained small amounts (5–10%) of the 1,4-adducts. We were unable to conclusively establish whether these products are formed under kinetic control or result from isomerization of the initially formed adducts. The amount of each product was determined, where possible, from nonoverlapping peaks in the proton NMR spectrum of the reaction mixture immediately after mixing.

## Discussion

From the data in Table I, it is clear that substituting a hydrogen on 1,3-butadiene by a methyl group increases the rate of addition. This increase in rate is about the same as that found by progressively substituting the hydrogens on ethylene by methyl groups.

Substituent effects are somewhat more difficult to analyze for dienes compared to monoalkenes, since there exist two possible sites of attack by the electrophile. Thus

(4) (a) G. H. Schmid, C. L. Dean, and D. G. Garratt, *Can. J. Chem.*, **54**, 1253 (1976); (b) D. G. Garratt and G. H. Schmid, *J. Org. Chem.*, **42**, 1776 (1977).

(5) D. G. Garratt, Ph.D. Thesis, University of Toronto, 1975.

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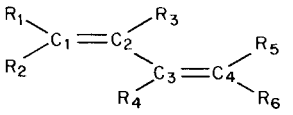
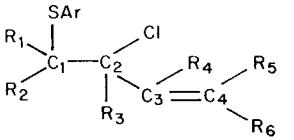
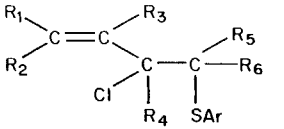
Table II. NMR Data of the 1,2-Adducts of 4-Chlorobenzenesulfenyl Chloride with 1,3-Butadiene and Several Methyl Derivatives under Conditions of Kinetic Control



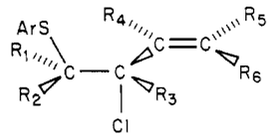




| $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | no. | $CH_3$ | $CH_2S$ | CHS | CHCl | $=CH_2$ | =CH | $=CHCH_3$ | $CH_3$ | $CH_2S$ | CHS | CHCl | $=CH_2$ | =CH | $=CHCH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | H | H | H | 1 | | 3.23 dd<br>3.33 dd | | 4.37 | 5.84 dq | 5.23 m | | | | | | | | |
| H | H | H | H | H | $CH_3$ | 5 | 1.65 dd[c] | 3.23 dq | | 4.37 dq | | | 5.32<br>4.7 m | 1.36 d[b] | | 3.4 m | 4.22–<br>4.50 m | 5.15 m | 6.00 m | |
| H | H | H | H | $CH_3$ | H | 4 | 1.53 dd[c] | 3.23 dq | | 4.74 da | | | 5.38 | 1.38 d[b] | | 3.52 dq | 4.45 | 5.20–<br>5.48 m | 6.1 dd | |
| H | H | $CH_3$ | H | H | H | 2 | 1.75 s[d] | 3.38 s | | | 5.06 dd | 6.00 dd | | 1.76 m[d] | 3.18–<br>3.53 dq | | | 4.41 q | | |
| H | H | $CH_3$ | $CH_3$ | H | H | 3 | 1.8 d[d] | 3.46 q | | | 5.13 | | | | | | | | | |
| H | H | H | H | $CH_3$ | $CH_3$ | 6 | 1.62 d[c]<br>1.69 d[a,c] | 3.25 | | 4.68 ddd | | 5.17[a] | | | | | | | | |
| H | $CH_3$ | H | H | $CH_3$ | H | 9 | 1.4 d[b]<br>1.6 d[c] | | 3.55 dq | 4.84 dd | | | 5.45–<br>4.92 m | | | | | | | |
| $CH_3$ | H | H | H | H | $CH_3$ | 11 | 1.36 d[b]<br>1.65 d[c] | | 3.35 dq | 4.38 dd | | | 5.32–<br>5.9 m | | | | | | | |
| $CH_3$ | H | H | H | $CH_3$ | H | 10 | 1.36 d[b]<br>1.73 d[c] | | 3.4 dq | 4.46 m | | | 5.45–<br>5.93 m | 1.40 d[b]<br>1.61 d[c] | | 3.32 q | 4.71 m | | | 5.45–<br>5.87 m |
| H | H | H | $CH_3$ | $CH_3$ | H | 7 | 1.71 s[a,c]<br>1.52 d[a] | 3.16 q<br>3.39 q | | 4.92 q | | | 5.45 q[a] | 1.76 s[e]<br>1.42 d[b] | | 3.39 q | | 5.38 dd<br>5.21 dd | 6.12 dd | |
| H | H | H | $CH_3$ | H | $CH_3$ | 8 | 1.63 s[a,c]<br>1.58 d[a] | 3.30 q<br>3.23 q | | 4.42 q | | | 5.53 q[a] | 1.76 s[e]<br>1.44 d[b] | | 3.36 q | | 5.34 dd<br>5.12 dd | 5.99 dd | |
| H | H | $CH_3$ | H | H | $CH_3$ | 12 | 1.66 d[c]<br>1.74 s[e] | 3.39 s | | | | | 5.68 | 1.66 s[d]<br>1.54 d[b] | | | | 5.02 d[a] | | |

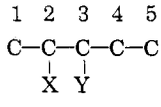
[a] Further small splittings. [b] $CH_3CHSAr$. [c] $CH_3CH=$. [d] $CH_3C(R)=$. [e] $CH_3CHCl$.

Table III. Observed $^{13}C$ NMR Chemical Shifts for a Series of β-Chloroalkyl γ,δ-Unsaturated 4-Chlorophenyl Sulfides



| structural assignment | | | | | | configuration | chemical shift assignments, δ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | | $C_{SAr}$ | $C_{Cl}$ | $C_{R_4}$ | $C_{R_{5,6}}$ | |
| H | H | H | H | H | H | | 42.10 | 60.16 | 136.48 | 118.75 | |
| H | H | H | H | H | Me | *Z* | 42.10 | 54.08 | 133.43 | | $R_6$ = 13.21 |
| H | H | H | H | Me | H | *E* | 42.34 | 60.51 | 130.38 | 130.08 | $R_5$ = 17.44 |
| H | H | H | Me | H | H | | 39.96 | 63.64 | | 116.50 | $R_4$ = 16.51 |
| H | H | Me | H | H | H | | 48.80 | 70.13 | 140.95 | 115.05 | $R_3$ = 28.97 |
| H | Me | H | H | H | H | 2-*RS*,3-*SR* | 54.17 | 66.17 | | 118.27 | $R_2$ = 17.15 |
| Me | H | H | H | H | H | 2-*RS*,3-*SR* | 49.34 | 64.69 | | 119.55 | $R_1$ = 15.56 |
| H | H | H | H | Me | Me | | 42.79 | 56.44 | 124.49 | 138.66 | $R_5$ = 25.57, $R_6$ = 18.25 |
| H | H | H | Me | H | Me | *Z* | 39.74 | 56.69 | 134.66 | 126.56 | $R_4$ = 17.01, $R_6$ = 13.11 |
| H | H | H | Me | Me | H | *E* | 40.19 | 66.70 | 133.73 | 126.17 | $R_4$ = 13.43, $R_5$ = 10.44 |
| H | H | Me | H | Me | H | *E* | 49.67 | 70.62 | | | $R_3$ = 28.14, $R_5$ = 17.53 |
| H | H | Me | Me | H | H | | 47.32 | 72.76 | 139.10 | 114.35 | $R_3$ = 28.33, $R_4$ = 19.24 |
| Me | H | H | H | H | Me | 2-*SR*,3-*RS*,*Z* (**17**) | 49.58 | 58.30 | 130.17 | 126.15 | $R_1$ = 15.52, $R_6$ = 13.36 |
| Me | H | H | H | Me | H | 2-*SR*,3-*RS*,*E* (**16**) | 50.20 | 60.20 | 132.90 | 126.75 | $R_2$ = 17.77, $R_6$ = 13.03 |
| H | Me | H | H | Me | H | 2-*RS*,3-*SR*,*E* (**14**) | 50.83 | 66.78 | 130.06 | 129.67 | $R_2$ = 17.53, $R_5$ = 17.53 |
| Me | H | Me | H | H | H | 2-*RS*,3-*SR* | 56.78 | 74.80 | 139.74 | 115.77 | $R_1$ = 18.59, $R_3$ = 28.14 |
| H | Me | Me | H | H | H | 2-*RS*,3-*SR* | 56.30 | 74.61 | 141.65 | 114.80 | $R_2$ = 18.31, $R_3$ = 25.73 |
| H | Me | H | Me | H | H | 2-*RS*,3-*SR* | 47.27 | 76.12 | | 116.07 | $R_2$ = 17.53, $R_4$ = 26.12 |
| H | Me | H | H | H | Me | 2-*RS*,3-*SR*,*Z* (**15**) | 49.77 | 64.93 | 131.35 | 129.09 | $R_1$ = 15.77, $R_5$ = 17.63 |

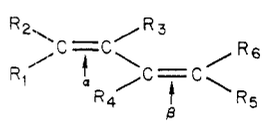
Table IV. Observed $^{13}C$ NMR Chemical Shifts for a Series of Configurational Diastereoisomers: 2-*RS*,3-*RS*, and 2-*RS*,3-*SR* 2,3-Disubstituted Butanes and Pentanes[a]

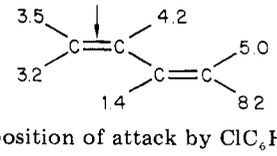


| compound[b] | | configuration | chemical shifts, δ | | | | |
|---|---|---|---|---|---|---|---|
| X | Y | | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ |
| Cl | Cl | 2-*RS*,3-*RS* | 19.95 | 60.47 | 60.47 | 19.95 | |
| | | 2-*RS*,3-*SR* | 22.13 | 61.62 | 61.62 | 22.13 | |
| Br | Br | 2-*RS*,3-*RS* | 20.59 | 52.33 | 52.33 | 20.59 | |
| | | 2-*RS*,3-*SR* | 25.34 | 53.94 | 53.94 | 25.34 | |
| Br | Br | 2-*RS*,3-*RS* | 21.59 | 52.10 | 62.07 | 27.48 | 12.69 |
| | | 2-*RS*,3-*SR* | 25.29 | 51.73 | 63.09 | 30.48 | 11.87 |
| ArS | Cl | 2-*RS*,3-*RS* | 14.80 | 49.95 | 59.62 | 18.82 | |
| | | 2-*RS*,3-*SR* | 17.06 | 51.25 | 61.40 | 23.29 | |
| ArS | Cl | 2-*RS*,3-*RS* | 16.10 | 49.89 | 67.68 | 26.06 | 11.81 |
| | | 2-*RS*,3-*SR* | 16.75 | 49.46 | 68.43 | 29.44 | 11.58 |
| Ar'S | Cl | 2-*RS*,3-*RS* | 15.61 | 47.15 | 66.56 | 26.78 | 11.74 |
| | | 2-*RS*,3-*SR* | 15.76 | 46.89 | 67.72 | 29.57 | 11.60 |
| Ar'Se | Cl | 2-*RS*,3-*RS* | 16.25 | 44.00 | 67.91 | 27.77 | 11.90 |
| | | 2-*RS*,3-*SR* | 16.48 | 43.35 | 68.53 | 29.96 | 11.80 |
| Cl | ArS | 2-*RS*,3-*RS* | 19.71 | 59.56 | 58.58 | 22.65 | 12.49 |
| | | 2-*RS*,3-*SR* | 22.91 | 60.69 | 59.83 | 24.95 | 11.38 |
| Cl | Ar'S | 2-*RS*,3-*RS* | 20.06 | 58.13 | 55.35 | 22.05 | 12.34 |
| | | 2-*RS*,3-*SR* | 21.97 | 59.72 | 56.77 | 24.89 | 11.80 |
| Cl | Ar'Se | 2-*RS*,3-*RS* | 21.12 | 59.37 | 53.36 | 22.66 | 13.13 |
| | | 2-*RS*,3-*SR* | 22.93 | 60.33 | 54.67 | 25.27 | 12.39 |
| PhSe | Cl | 2-*RS*,3-*RS* | 15.82 | 45.89 | 61.12 | 19.82 | |
| | | 2-*RS*,3-*SR* | 18.69 | 46.44 | 62.88 | 24.16 | |

[a] Data from ref 5. [b] Ar = 4-chlorophenyl; Ar' = 2,4-dinitrophenyl; Ph = phenyl.

replacement of a hydrogen by a methyl group at, for example, $R_3$ will show a different effect if attack occurs at the α double bond than if attack occurs at the β double bond. From both the rates of addition and the initially formed products, it is possible to calculate the relative rate increase of replacing a hydrogen by a methyl group at any of the six possible locations. The rate factors are shown below:





↓ = position of attack by $ClC_6H_4SCl$

Table V. Product Composition

| diene | initial product composition[a] | | product of isomerization |
|---|---|---|---|
| $CH_2$=CHCH=$CH_2$ (1) | $ArSCH_2CHClCH=CH_2$ (>95%) | | none |
| $CH_2$=$C(CH_3)CH=CH_2$ (2) | $ArSCH_2C(CH_3)ClCH=CH_2$ (72%) | $CH_2=C(CH_3)CHClCH_2SAr$ (23%) | (*E*)- and (*Z*)-$ClCH_2C(CH_3)$=$CHCH_2SAr$ |
| $CH_2$=$C(CH_3)C(CH_3)$=$CH_2$ (3) | $ArSCH_2C(CH_3)ClC(CH_3)=CH_2$ (>95%) | | (*E*)- and (*Z*)-$ClCH_2C(CH_3)=C(CH_3)CH_2SAr$ |
| (*Z*)-$CH_3CH$=$CHCH$=$CH_2$ (4) | (*Z*)-$ArSCH_2CHClCH=CHCH_3$ (73%) | $CH_3CH(SAr)CHClCH=CH_2$ (27%) | (*E*)-$ArSCH_2CH=CHCHClCH_3$ |
| (*E*)-$CH_3CH$=$CHCH$=$CH_2$ (5) | (*E*)-$ArSCH_2CHClCH=CHCH_3$ (60%) | $CH_3CH(SAr)CHClCH=CH_2$ (35%) | (*E*)-$ArSCH_2CH=CHCHClCH_3$ |
| $CH_2$=$CHCH=C(CH_3)_2$ (6) | $ArSCH_2CHClCH=C(CH_3)_2$ (>95%) | | (*E*)-$ArSCH_2CH=CHCCl(CH_3)_2$ |
| (*Z*)-$CH_2$=$CHC(CH_3)$=$CHCH_3$ (7) | (*Z*)-$ArSCH_2CHClC(CH_3)=CHCH_3$ (53%) | $CH_2=CHCCl(CH_3)CH(SAr)CH_3$ (45%) | (*E*)-$ClCH_2CH=C(CH_3)CH(SAr)CH_3$ |
| (*E*)-$CH_2$=$CHC(CH_3)$=$CHCH_3$ (8) | (*E*)-$ArSCH_2CHClC(CH_3)=CHCH_3$ (53%) | $CH_2=CHCCl(CH_3)CH(SAr)CH_3$ (44%) | (*E*)-$CH_3CHClCH=CHCH(ArS)CH_3$ |
| (*Z*,*Z*)-$CH_3CH$=$CHCH$=$CHCH_3$ (9) | (*Z*)-$ArSCH(CH_3)CHClCH=CHCH_3$ (>95%) | | (*E*)-$CH_3CHClCH=CHCH(ArS)CH_3$ |
| (*E*,*Z*)-$CH_3CH$=$CHCH$=$CHCH_3$ (10) | (*Z*)-$ArSCH(CH_3)CHClCH=CHCH_3$ (28%) | (*E*)-$ArSCH(CH_3)CHClCH=CHCH_3$ (67%) | |
| (*E*,*E*)-$CH_3CH$=$CHCH$=$CHCH_3$ (11) | (*E*)-$ArSCH(CH_3)CHClCH=CHCH_3$ (>95%) | | (*E*)-$CH_3CHClCH=CHCH(ArS)CH_3$ |
| (*E*)-$CH_2$=$C(CH_3)CH$=$CHCH_3$ (12) | (*E*)-$ArSCH_2C(CH_3)ClCH=CHCH_3$ (73%) | $CH_3CH(SAr)CHClC(CH_3)=CH_2$ (22%) | (*E*)- and (*Z*)-$ArSCH_2(CH_3)C=CHCHClCH_3$ |

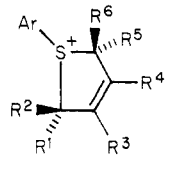
[a] Dienes 2, 3, 5, 7, 8, 10, 11, and 12 also formed small amounts (<10%) of 1,4-adducts.

Thus if $R_3$ is a methyl group, the rate of addition is calculated to be about 4.2 relative to that of 1,3-butadiene.

The effects are not strictly multiplicative but are essentially reflective of the effect of substitution. It is seen that $k_2$(trans) is somewhat larger than the corresponding $k_2$(cis). This is opposite to what is normally observed for alkyl-substituted alkenes where $k_2$(cis) $\geq$ $k_2$(trans), but is similar to the cases involving aryl-substituted alkenes.[7] A remote trans-oriented methyl group (i.e., $R_5$ = $CH_3$) causes the largest rate increase.

A slight preference for addition to the least substituted double bond is found. This is in contrast to the addition to simple alkenes where the usual order of reactivity is tetrasubstituted > trisubstituted > cis-1,2-disubstituted > 1,1-disubstituted $\approx$ trans-1,2-disubstituted > monosubstituted alkene.[4a] Similar results have been reported for the bromination of dienes.[3a]

The effect of substituents on the rate, the stereospecific anti addition, and the preferential 1,2-Markownikoff regiochemistry are all in accord with the usual mechanism of addition of arenesulfenyl chlorides which involves rate- and product-determining transition states that resemble a thiiranium ion.[8] The increase in rate caused by a methyl group on the $\beta$ double bond is similar to the effect on the rate of substituents in the phenyl ring of styrene derivatives.[9] Thus there is charge delocalization into either the double bond (for dienes) or the phenyl ring (for styrenes) in the rate-determining transition state. This implies that for both reactions the structure of the rate-determining transition states, while bridged, is unsymmetrical. Further the effect of substituents suggests that addition occurs to only one double bond. This rules out the rate-determining formation of a substituted tetramethylenesulfonium ion intermediate (**17**).



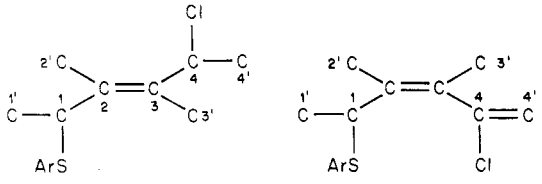

**17**

The similarity between additions to conjugated dienes and styrenes is also evident from a comparison of the stereochemistry of the 1,2 addition of chlorine, bromine, and arenesulfenyl chloride. For both, the addition of chlorine is nonstereospecific;[3c,10] the addition of bromine is anti-stereoselective;[3a,11] and the addition of arenesulfenyl chloride is anti-stereospecific.[9]

Our rate and product data indicate that arenesulfenyl chlorides react with only one of the two double bonds of a conjugated diene to form the 1,2-adduct by anti-stereospecific addition. The results are in accord with the accepted mechanism for additions of arenesulfenyl chlorides to simple alkenes.

(7) G. H. Schmid and D. G. Garratt, *Can. J. Chem.*, **52**, 1807 (1974).
(8) For a review of the additions of arenesulfenyl chlorides to alkenes, see G. H. Schmid, *Top. Sulfur Chem.*, **3**, 100 (1977).
(9) (a) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1201 (1956); (b) K. Izawa, T. Okuyama, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **47**, 1480 (1974); (c) G. H. Schmid and V. J. Nowlan, *Can. J. Chem.*, **54**, 695 (1976).
(10) H. W. Leung, Ph.D. Thesis, University of Toronto.
(11) (a) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1469 (1969); (b) R. C. Fahey and J.-J. Schneider, *ibid.*, **90**, 4429 (1968).
(12) G. H. Schmid, V. M. Csizmadia, V. J. Nowland, and D. G. Garratt, *Can. J. Chem.*, **50**, 2457 (1972).

Table VI. Observed $^{13}C$ NMR Chemical Shifts for a Series of (*E*)- and (*Z*)-δ-Chloroalkyl β,γ-Unsaturated 4-Chlorophenyl Sulfides



*E* *Z*

| structure assignment | | | | | chemical shift assignments, δ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1′ | 2′ | 3′ | 4′ | | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_{1'}$ | $C_{2'}$ | $C_{3'}$ | $C_{4'}$ |
| H, H | H | H | Me, H<br>H, Me | *E* | 35.94 (t) | | | 56.68 (d) | | | | 25.02 (q) |
| H, H | Me | H | H, H | *E* | 40.10 (t) | | | 51.38 (t) | | 15.16 (q) | | |
| H, H | H | H | Me, Me | *E* | 36.41 (t) | 123.09 (d) | 139.88 (d) | 67.14 (s) | | | | 32.03 (q) |
| H, H | H | Me | Me, H<br>H, Me | *E* | 40.12 (t) | 122.70 (d) | 141.69 (s) | 52.24 (d) | | | 12.25 (q) | 18.94 (q) |
| H, H | Me | H | Me, H<br>H, Me | *E* | 44.09 (t) | | | 53.48 (d) | | 15.30 (q) | | 25.63 (q) |
| H, H | Me | H | Me, H<br>H, Me | *Z* | 36.77 (t) | | | 53.19 (d) | | 22.48 (q) | | 25.77 (q) |
| H, H | Me | Me | H, H | *E* | 39.59 (t) | | | 46.35 (t) | | 16.73 (q) | 17.60 (q) | |
| H, H | Me | Me | H, H | *Z* | 38.76 (t) | | | 45.50 (t) | | 17.26 (q) | 18.64 (q) | |
| Me, H<br>H, Me | H | H | Me, H<br>H, Me | *E* | 45.45 (d) | 132.59 (d) | 132.94 (d) | 56.96 (d) | 19.88 (q) | | | 25.18 (q) |
| Me, H<br>H, Me | H | H | H, Me<br>Me, H | *E* | 45.30 (d) | 132.41 (d) | 132.70 (d) | 56.82 (d) | 19.99 (q) | | | 25.08 (q) |

Table VII. Analytical Data for the Adducts of 4-Chlorobenzenesulfenyl Chloride and Dienes

| diene adduct (s) | found | | | calcd | | |
|---|---|---|---|---|---|---|
| | C | H | S | C | H | S |
| 2-methyl-1,3-butadiene | 53.25 | 4.96 | 13.13 | 53.45 | 4.89 | 12.97 |
| 1,3-dimethyl-1,3-butadiene | 55.17 | 5.27 | 12.69 | 55.18 | 5.40 | 12.27 |
| (*Z*)-1,3-pentadiene | 53.52 | 4.88 | 13.27 | 53.45 | 4.89 | 12.97 |
| (*E*)-1,3-pentadiene | 53.68 | 4.86 | 13.23 | 53.45 | 4.89 | 12.97 |
| (*E*)-3-methyl-1,3-pentadiene | 55.15 | 5.27 | 12.48 | 55.18 | 5.40 | 12.27 |
| (*Z*)-3-methyl-1,2-pentadiene | 54.91 | 5.51 | 12.50 | 55.18 | 5.40 | 12.27 |
| (*E,E*)-2,4-hexadiene | 55.19 | 5.24 | 12.61 | 55.18 | 5.40 | 12.27 |
| (*Z,E*)-2,4-hexadiene | 55.11 | 5.15 | 12.37 | 55.18 | 5.40 | 12.27 |
| (*Z,Z*)-2,4-hexadiene | 54.99 | 5.46 | 12.31 | 55.18 | 5.40 | 12.27 |
| 4-methyl-1,3-pentadiene | 55.27 | 5.26 | 12.94 | 55.18 | 5.40 | 12.27 |
| (*E*)-2-methyl-1,3-pentadiene | 55.05 | 5.35 | 12.95 | 55.18 | 5.40 | 12.27 |

## Experimental Section

The dienes were obtained commercially and their purity was verified by GLC and NMR. Microanalyses were carried out by A.B. Gygli Microanalysis Laboratory, Toronto, Ontario, Canada.

4-Chlorobenzenesulfenyl chloride was prepared as previously described.[12] 1,1,2,2-Tetrachloroethane was purified as previously described.[12] Kinetics and product compositions were determined as previously described. The elemental analyses are reported in Table VII.

**Acknowledgment.** Continued financial support from the National Research Council of Canada is gratefully acknowledged. A University of Toronto special open fellowship (1973–1974) and an NRCC postgraduate scholarship (1974–1976) to D.G.G. and a Government of Iran Minister of Science and Higher Education Scholarship to S.Y. are also very much appreciated.

**Registry No.** 1, 106-99-0; 2, 78-79-5; 3, 513-81-5; 4, 1574-41-0; 5, 2004-70-8; 6, 926-56-7; 7, 2787-45-3; 8, 2787-43-1; 9, 6108-61-8; 10, 5194-50-3; 11, 5194-51-4; 12, 926-54-5; 14, 72622-92-5; 15, 72622-93-6; 16, 72622-94-7; 17, 72622-95-8; 1-chloro-4-[(2-chloro-3-butenyl)thio]benzene, 72622-96-9; (*Z*)-1-chloro-4-[(2-chloro-3-pentenyl)thio]benzene, 72622-97-0; (*E*)-1-chloro-4-[(2-chloro-3-pentenyl)thio]benzene, 72622-98-1; 1-chloro-4-[(2-chloro-2-methyl-3-butenyl)thio]benzene, 72622-99-2; 1-chloro-4-[(2-chloro-2,3-dimethyl-3-butenyl)thio]benzene, 72623-00-8; 1-chloro-4-[(2-chloro-4-methyl-3-pentenyl)thio]benzene, 72623-01-9; (*E*)-1-chloro-4-[(2-chloro-3-methyl-3-pentenyl)thio]benzene, 72623-02-0; (*Z*)-1-chloro-4-[(2-chloro-3-methyl-3-pentenyl)thio]benzene, 72623-03-1; (*Z*)-1-chloro-4-[(2-chloro-2-methyl-3-pentenyl)thio]benzene, 72623-04-2; *erythro*-1-chloro-4-[(2-chloro-1-methyl-3-butenyl)thio]benzene, 72623-05-3; 1-chloro-4-[(2-chloro-3-methyl-3-butenyl)thio]benzene, 72623-06-4; *threo*-1-chloro-4-[(2-chloro-1,2-dimethyl-3-butenyl)thio]benzene, 72623-07-5; *erythro*-1-chloro-4-[(2-chloro-1,3-dimethyl-3-butenyl)thio]benzene, 72623-08-6; *threo*-1-chloro-4-[(2-chloro-1-methyl-3-butenyl)thio]benzene, 72623-09-7; (*E*)-1-chloro-4-[(2-chloro-2-methyl-3-pentenyl)thio]benzene, 72623-10-0; *erythro*-1-chloro-4-[(2-chloro-1,2-dimethyl-3-butenyl)thio]benzene, 72657-77-3; *threo*-2,3-dichlorobutane, 2211-67-8; *erythro*-2,3-dichlorobutane, 4028-56-2; *threo*-2,3-dibromobutane, 598-71-0; *erythro*-2,3-dibromobutane, 5780-13-2; *threo*-1-chloro-4-[(2-chloro-1-methylpropyl)thio]benzene, 72623-11-1; *erythro*-1-chloro-4-[(2-chloro-1-methylpropyl)thio]benzene, 72623-12-2; *threo*-[(2-chloro-1-methylpropyl)seleno]benzene, 69924-54-5; *erythro*-[(2-chloro-1-methylpropyl)seleno]benzene, 69924-55-6; (*E*)-1-chloro-4-[(4-chloro-2-pentenyl)thio]benzene, 72623-13-3; (*E*)-1-chloro-4-[(4-chloro-2-methyl-2-butenyl)thio]benzene, 27995-58-0; (*E*)-1-chloro-4-[(4-chloro-4-methyl-2-pentenyl)thio]benzene, 72623-14-4; (*E*)-1-chloro-4-[(4-chloro-3-methyl-2-pentenyl)thio]benzene, 72623-15-5; (*E*)-1-chloro-4-[(4-chloro-2-methyl-2-pentenyl)thio]benzene, 72623-16-6; (*Z*)-1-chloro-4-[(4-chloro-2-methyl-2-pentenyl)thio]benzene, 72638-59-6; (*E*)-1-chloro-4-[(4-chloro-2,3-dimethyl-2-butenyl)thio]benzene, 27995-56-8; (*Z*)-1-chloro-4-[(4-chloro-2,3-dimethyl-2-butenyl)thio]benzene, 27995-55-7; (*E*)-*threo*-1-chloro-4-[(4-chloro-1-methyl-2-pentenyl)thio]benzene, 67145-79-3; (*E*)-*erythro*-1-chloro-4-[(4-chloro-1-methyl-2-pentenyl)thio]benzene, 67145-80-6; 4-chlorobenzenesulfenyl chloride, 933-01-7.