of 1:1:1:1:75 were prepared and divided among eight ampules as before. When the vinylarenes were 1-, 2-, or 9-vinylanthracene or 1-vinylpyrene, about 5 mol % benzoyl peroxide was added to seven of the ampules before sealing. This was done because the vinylanthracenes and 1-vinylpyrene all seemed to undergo photoinduced dimerization reactions. The other compounds were all initiated by light. One ampule was always reserved as a reference solution. Seven ampules were then allowed to react at 70.0 °C in a constant-temperature bath for times ranging from 10 to 40 h. From 15 to 80% of the vinylarenes reacted in this period. When photolytic initiation was used, a 275-W sun lamp was placed 10 cm above the tubes in the bath.

The usual calculations of the relative rates[35] were modified in the following manner. The areas of the olefins and thiophenol relative to the internal standard are calculated by

$$X = A/S \tag{12}$$

where X is a relative area, A is an actual measured area, and S is the area of the internal standard. Using the normal method of analysis, the rate ratio is given by

$$\frac{R_1}{R_2} = \frac{\ln\left[\frac{X_1^{\,i}}{X_1^{\,f}}\right]}{\ln\left[\frac{X_2^{\,i}}{X_2^{\,f}}\right]} \tag{13}$$

The subscripts refer to olefins 1 and 2 and the superscripts i and f denote unreacted and reacted samples, respectively. If olefin 1 is a vinylarene, the numerator may be calculated as follows

$$\frac{X_1^{\,i}}{X_1^{\,f}} = \frac{M_1}{M_1 - M_s\cdot\left[1 - \frac{X_s^{\,f}}{X_s^{\,i}}\right] + M_2\cdot\left[1 - \frac{X_2^{\,f}}{X_2^{\,i}}\right]} \tag{14}$$

where the M's are the number of moles of each of the indicated species that were initially weighed out in the preparation of the reaction mixture. Subscripts refer to olefins 1 and 2 and to thiophenol S. Expression 14 is then substituted into eq 13 and the rate ratio is calculated as before.

Acknowledgment. We wish to thank the OSU Computing Center for their generous donation of the computer time necessary for carrying out this project.

Registry No.—Thiophenol, 108-98-5.

References and Notes

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Effect of Acetylene Structure on the Rates and Products of Addition of 4-Chlorobenzenesulfenyl Chloride†

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The rates and products of addition of 4-chlorobenzenesulfenyl chloride to acetylene and 12 alkyl-substituted derivatives have been determined in 1,1,2,2-tetrachloroethane at 25 °C. The effect of the alkyl groups on the rate of addition to 10 of the 13 alkynes can be correlated by means of the Taft equation: $\log k_2 = -4.47\Sigma\sigma^* + 1.64$. The three compounds that do not lie on the line contain *tert*-butyl substituents. Polar effects of the substituents on the rates are dominant and steric effects are important only for *tert*-butyl groups. The product regiochemistry, however, is determined by the steric bulk of the substituent. The results are consistent with a mechanism involving bridged thiirenium ion-like rate and product determining transition states.

The electrophilic addition of arenesulfenyl chlorides to alkynes has received much less attention than the analogous addition to alkenes. The majority of work on this subject has been concentrated on the addition to phenyl-substituted alkynes.[2-4] We now wish to present the results of a systematic study of the polar and steric effects of alkyl groups on the rate and products of addition of 4-chlorobenzenesulfenyl chloride to alkynes in 1,1,2,2-tetrachloroethane at 25 °C.

† Reactions of Sulfenyl Halides and Their Derivatives. 14. For part 13 see ref 1.

Results and Discussion

Effect of Alkyl Groups on the Rate of Addition. The rates of addition of 4-chlorobenzenesulfenyl chloride to acetylene (1) and 12 alkyl-substituted derivatives (2–13) were measured by following the disappearance of the 4-chloro-

Table I. Bimolecular Specific Rate Constants for the Addition of 4-Chlorobenzenesulfenyl Chloride to Alkynes in 1,1,2,2-Tetrachloroethane at 25 °C

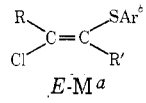
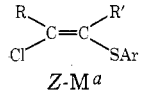
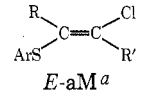
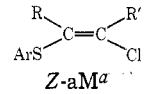
Registry no.	Alkyne	k_2, M^{-1} s^{-1}	k_{rel}
74-86-2	HC≡CH (1)	2.31 ± 0.02 × 10^{-3}	1.0
74-99-7	CH_3C≡CH (2)	0.424 ± 0.002	183
107-00-6	C_2H_5C≡CH (3)	0.993 ± 0.002	429
598-23-2	i-C_3H_7C≡CH (4)	1.52 ± 0.04	658
917-12-0	t-C_4H_9C≡CH (5)	1.02 ± 0.01	442
627-19-0	n-C_3H_7C≡CH (6)	0.912 ± 0.002	394
693-02-7	n-C_4H_9C≡CH (7)	0.961 ± 0.003	416
503-17-3	CH_3C≡CCH_3 (8)	75.9 ± 0.4	3.29 × 10^4
627-21-4	C_2H_5C≡CCH_3 (9)	132 ± 1	5.71 × 10^4
21020-27-9	i-C_3H_7C≡CCH_3 (10)	137 ± 1	5.93 × 10^4
999-78-0	t-C_4H_9C≡CCH_3 (11)	31.8 ± 0.1	1.38 × 10^4
928-49-4	C_2H_5C≡CC_2H_5 (12)	233 ± 1	1.00 × 10^5
17530-24-4	t-C_4H_9C≡C-t-C_4H_9 (13)	0.329 ± 0.003	142

Table II. Cumulative Effect of Methyl and Ethyl Groups on the Addition

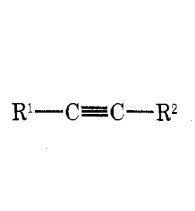
Methyl substituted series	k_{rel}	Ethyl substituted series	k_{rel}	k_{rel}[a]
HC≡CH	1.0	HC≡CH	1.0	1.0
HC≡CCH_3	183	HC≡CC_2H_5	429	274
CH_3C≡CCH_3	3.29 × 10^4 = $(181)^2$	C_2H_5C≡CC_2H_5	1.00 × 10^5 = $(316)^2$	2.08 × 10^4 = $(144)^2$

[a] Data taken from ref 7.

Table III. Kinetically Controlled Product Distribution for the Addition of 4-Chlorobenzenesulfenyl Chloride to Unsymmetrical Alkynes

		Product composition			
					
R	R′	E-M[a]	Z-M[a]	E-aM[a]	Z-aM[a]
CH_3	H (2)	14	0	86	0
C_2H_5	H (3)	10	0	90	0
i-Pr	H (4)	27	0	73	0
t-Bu	H (5)	0	0	100	0
n-C_3H_7	H (6)	16	0	84	0
n-C_4H_9	H (7)	20	0	80	0
CH_3	C_2H_5 (9)	60	0	40	0
CH_3	i-Pr (10)	48	0	52	0
CH_3	t-Bu (11)	12	5	76	7

[a] M = Markownikoff isomer is the one in which the chlorine is bonded to the carbon atom whose Taft inductive substituent constant, σ^*, is the more negative. [b] Ar = 4-ClC_6H_4.



	R^1	R^2		R^1	R^2
1	H	H	8	CH_3	CH_3
2	CH_3	H	9	CH_3	C_2H_5
3	C_2H_5	H	10	CH_3	i-C_3H_7
4	i-C_3H_7	H	11	CH_3	t-C_4H_9
5	t-C_4H_9	H	12	C_2H_5	C_2H_5
6	n-C_3H_7	H	13	t-C_4H_9	t-C_4H_9
7	n-C_4H_9	H			

benzenesulfenyl chloride absorption at 392.5 nm. The stopped-flow technique using a Durrum-Gibson spectrophotometer was used for all the compounds except acetylene, whose reaction was monitored by conventional techniques using a Cary 16 spectrophotometer. The additions were found to follow normal second-order kinetics, first order in both alkyne and sulfenyl halide to 80% completion of the reaction. The second-order rate constants are given in Table I.

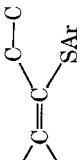
From the rate data in Table I it is clear that the substitution of one hydrogen on acetylene by an alkyl group leads to a rate enhancement of several hundred. Replacement of both hydrogens leads to further rate enhancements. The rate constants follow the simple Taft correlation[5] as illustrated in Figure 1. Ten of the 13 points lie on a straight line whose equation is

$$\log k_2 = -4.47\sum\sigma^* + 1.64$$

The remaining three points, for compounds containing *tert*-butyl groups, lie off the line. Such a relationship implies that for methyl, ethyl, and isopropyl substituents, only their polar effects are important in the rate-determining transition state. Steric effects are important only when *tert*-butyl is a substituent. The fact that the point for di-*tert*-butylacetylene is way off the line further supports this view.

In accord with previous findings,[6] the rate of addition to alkynes is slower than to ethylenes. For the two series the rate difference is a maximum for the two parent compounds $k(CH_2$=$CH_2)/k$(HC≡CH) = 2.82 × 10^5. As the hydrogens are progressively substituted by alkyl groups the ratio k_{al}/k_{ac} diminishes. Thus the effect of alkyl substituents is greater upon the rate of addition to alkynes than to alkenes. Such a result is inconsistent with a radical mechanism. Rather it is consistent with the different extent of p character in the carbon atoms of the two bridged ions formed in the addition to alkynes and alkenes. The amount of p character in the carbon atoms is less in the rate-determining transition state for the addition to alkynes. Consequently the carbons are more electronegative and make a greater demand upon the electron-donating alkyl substituents.

Table IV. Observed Carbon-13 Magnetic Resonance Parameters for the Adducts of 4-Chlorobenzenesulfenyl Chloride to Disubstituted Alkynes



Registry no.	Compd		Chemical shifts, δ, ppm[a]					Coupling constants, Hz			
			C_3	C_2	C_1	C_1'	C_2'	C_3'	J_{C_3H}	J_{C_2H}	$J_{C_2'H}$	$J_{C_3'H}$
58866-30-1	$CH_3C(Cl)=C(SAr)CH_3$	E		24.48	133.51	124.23	21.65			130.1	129.7	
58866-31-2		Z		23.40	133.98	125.69	19.69			129.7	126.6	
58866-32-3	$CH_3C(Cl)=C(SAr)CH_2CH_3$	E		24.70	133.63	129.86	27.95	12.09		130.0	130.0	128.5
58866-33-4		Z		21.33	134.45	129.88	24.34	12.13				
58866-34-5	$CH_3C(Cl)=C(SAr)CH(CH_3)_2$	E		25.23	132.44	133.77	32.65	21.86				
58866-35-6		Z		22.22	133.28	134.47	30.22	20.26				
58866-36-7	$CH_3C(Cl)=C(SAr)C(CH_3)_3$	E		26.36	133.09	136.05	36.31	30.78				
58866-37-8		Z		24.75			34.57	30.29				
58866-38-9	$CH_3CH_2C(Cl)=C(SAr)CH_3$	E	12.83	30.83	141.43	123.31	21.66		126.9	129.0	129.4	
58866-39-0		Z	12.45	29.94	143.10	125.18	19.28		128.8	128.6	129.4	
58866-40-3	$CH_3CH_2C(Cl)=C(SAr)CH_2CH_3$	E	12.84	30.96	141.60	129.66	27.83	12.13				
58866-41-4		Z	12.37	29.46	142.88	130.34	24.37	12.18				
58866-42-5	$(CH_3)_2CHC(Cl)=C(SAr)CH_3$	E	20.89	33.49	146.71	122.00	20.51					
58866-43-6		Z	21.23	31.38	148.15	125.04	18.55					
58866-44-7	$(CH_3)_3CC(Cl)=C(SAr)CH_3$	E	29.78	38.56	148.24	123.03	21.57					
58866-45-8		Z	29.65	36.34	149.32	123.21	18.58					

[a] Chloroform-*d* solution 45% w/v, internal Me_4Si.

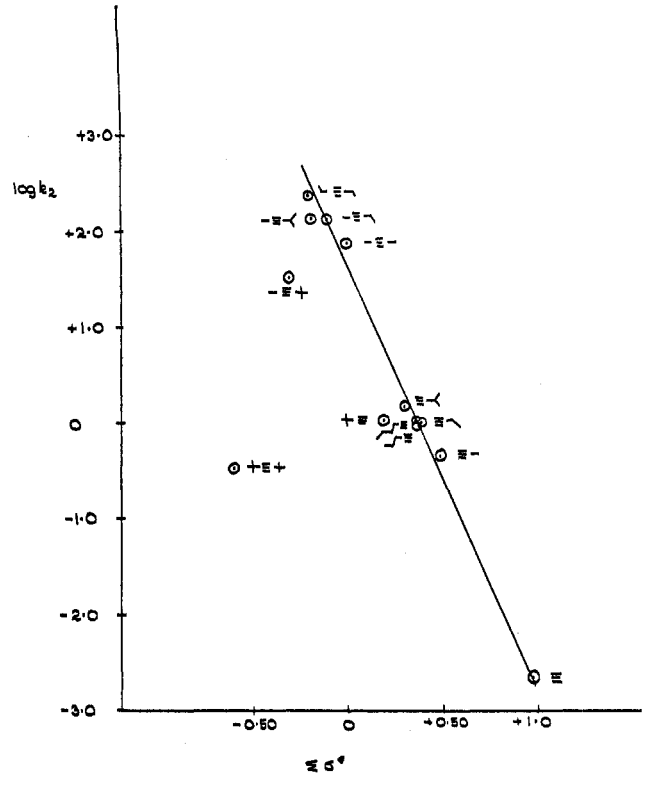
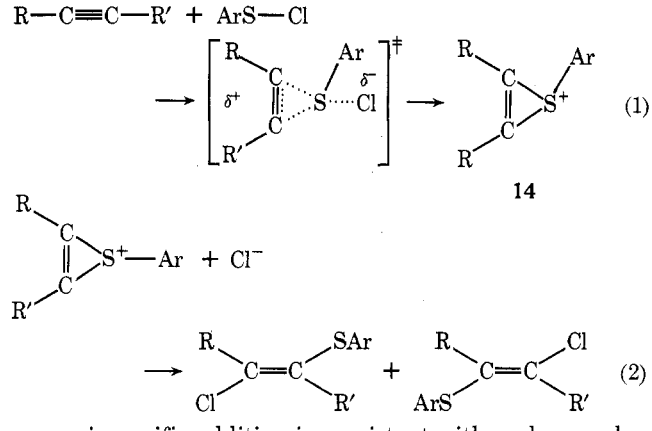


Figure 1. Plot of log k_2 vs. $\Sigma\sigma^*$ for addition of 4-chlorobenzenesulfenyl chloride to alkynes.

The mechanism of the addition of arenesulfenyl chlorides to alkynes has been postulated[2] to involve a bridged rate-determining transition state leading to a thiirenium ion 14 (eq 1). Chloride attack at either ring carbon of 14 results in formation of the adduct (eq 2). The anti stereospecific and

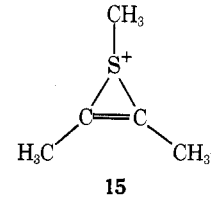


(1)

14

(2)

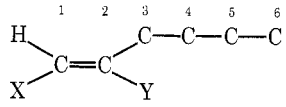
nonregiospecific addition is consistent with such a mechanism.[2,7] Recently the thiirenium ion 15 has been prepared in liquid SO_2 and its spectral properties have been reported.[8]



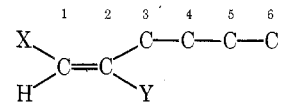
15

The data in Table I support this mechanism. The effect of progressively substituting the hydrogens on acetylene by methyl and ethyl is cumulative as shown in Table II. This indicates that the charge distribution is similar on both acetylenic carbon atoms in the rate-determining transition state, consistent with a bridged ion structure.

Table V. Observed Carbon-13 Magnetic Resonance Parameters for the Adducts of 4-Chlorobenzenesulfenyl Chloride to Terminal Alkynes



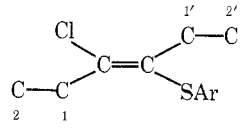
Z



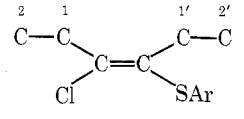
E

		Chemical shifts, δ, ppm					
		C_1	C_2	C_3	C_4	C_5	C_6
X = ArS Y = Cl							
$HC(SAr)=C(Cl)CH_3$	*E*	118.59 d	133.58 s	22.21 q			
$HC(SAr)=C(Cl)CH_2CH_3$	*E*	117.34 d	137.54 s	32.08 t	15.02 q		
$HC(SAr)=C(Cl)CH(CH_3)_2$	*E*	116.58 d	143.19 s	32.14 d	20.23 q		
$HC(SAr)=C(Cl)C(CH_3)_3$	*E*	115.37 d	148.29 s	39.78 s	31.28 q		
$HC(SAr)=C(Cl)(CH_2)_2CH_3$	*E*	116.54 d	139.62 s	37.45 t	27.38 t	14.02 q	
$HC(SAr)=C(Cl)(CH_2)_3CH_3$	*E*	116.48 d	140.24 s	36.34 t	26.88 t	22.31 t	13.88 q
X = Cl Y = SAr							
$HC(Cl)=C(SAr)CH_3$	*E*	119.56 d	129.53 s	18.30 q			
$HC(Cl)=C(SAr)CH_2CH_3$	*E*	119.32 d	130.67 s	29.38 t	14.21 t		
$HC(Cl)=C(SAr)CH(CH_3)_2$	*E*	119.17 d	131.56 s	31.29 d	20.47 q		
$HC(Cl)=C(SAr)C(CH_3)_3$	*E*	120.22 d	135.23 s	36.22 s	30.02 q		
$HC(Cl)=C(SAr)(CH_2)_2CH_3$	*E*	119.34 d	131.08 s	32.43 t	23.11 t	13.78 q	
$HC(Cl)=C(SAr)(CH_2)_3CH_3$	*E*	119.36 d	131.03 s	32.78 t	24.31 t	13.22 q	

Table VI. Observed Proton Magnetic Resonance Parameters for the Adducts of 4-Chlorobenzenesulfenyl Chloride to Disubstituted Alkynes



E



Z

		Chemical shifts, δ, ppm[a]				Coupling constants, Hz		
Compd		H_2	H_1	H_1'	H_2'	$J_{HCC=CCH}$	J_{12}	$J_{1'2'}$
$CH_3(Cl)=C(SAr)CH_3$	*E*		2.42 q	2.04 q		1.5		
	Z		2.21 q	1.82 q		1.0		
$CH_3C(Cl)=C(SAr)CH_2CH_3$	*E*		2.38 t	2.41 ct	1.03 t	1.2		7.0
	Z		2.19 t	2.28 qt	1.04 t	0.6		7.0
$CH_3C(Cl)=C(SAr)CH(CH_3)_2$	*E*		2.32 s	3.52 h'	1.00 d	≤0.4		6.5
	Z		2.15 s	3.42 h'	1.02 d			7.1
$CH_3C(Cl)=C(SAr)C(CH_3)_3$	*E*		2.47 s		1.38 s			
	Z		2.10 s		1.05 s			
$CH_3CH_2C(Cl)=C(SAr)CH_3$	*E*	1.12 t	2.80 qt	2.02 t		0.9	7.75	
	Z	1.15 t	2.50 qt	1.82 t		0.6	7.50	
$CH_3CH_2C(Cl)=C(SAr)CH_2CH_3$	*E*	1.12 t	2.80 q	2.40 q	1.04 t	≤0.7	7.50	7.50
	Z	1.16 t	2.48 q	2.21 q	1.08 t	0.6	7.21	7.26
$(CH_3)_2CHC(Cl)=C(SAr)CH_3$	*E*	1.11 d	3.50 h'	2.05 s		≤0.4	6.90	
	Z	1.15 d	3.67 h'	1.78 s			7.0	
$(CH_3)_3CC(Cl)=C(SAr)CH_3$	*E*	1.43 s		2.05 s				
	Z	1.18 s		1.74 s				

[a] Chloroform-*d* solution, 45% w/v, internal Me_4Si.

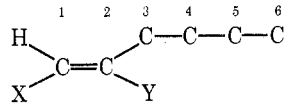
Effect of Alkyl Groups on Product Stereochemistry and Regiochemistry. The addition of arenesulfenyl chlorides to alkynes forms the 1:1 adducts in quantitative yield. No diadducts have ever been observed.[2-4] Previous work has established that the products of the reaction of arenesulfenyl chlorides and phenylacetylenes are formed by stereospecific anti and nonregiospecific addition. Similar results are found in this study based upon the nuclear magnetic resonance spectra of the products.

The kinetically controlled product distribution for the addition of 4-chlorobenzenesulfenyl chloride to the unsymmetrically substituted alkynes is given in Table III. The products of addition to the symmetrically substituted alkynes are those of anti stereospecific addition. No difference in product composition was observed in the presence or absence of oxygen and light.

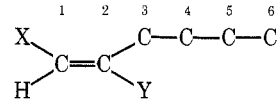
A catalytic amount of gaseous HCl was added to the reaction mixture of the addition to each unsymmetrical alkyne and it was observed that the ratio of Markownikoff to anti-Markownikoff products slowly changed over several weeks. In the absence of added HCl no isomerization was observed. These observations establish that the reaction products are formed under conditions of kinetic control. While HCl catalyzes the isomerization, it also causes decomposition of the products. This decomposition, while not serious initially, makes it impossible to establish the thermodynamically controlled product composition.

The percentage of each product was determined from the integrated area of nonoverlapping peaks in the proton spectrum (either 60 or 100 MHz) immediately after mixing. The products were identified by carbon-13 and proton magnetic resonance spectroscopy. The spectrum of each of the four

Table VII. Observed Proton Magnetic Resonance Parameters for the Adducts of 4-Chlorobenzenesulfenyl Chloride to Terminal Alkynes



Z



E

Registry no.			Chemical shifts, δ, ppm				
			H_1	H_3	H_4	H_5	H_6
	X = ArS; Y = Cl						
58866-46-9	$HC(SAr)=C(Cl)CH_3$	*E*	6.24 q	2.23 d			
58866-47-0		*Z*	5.97 q	2.09 d			
58866-48-1	$HC(SAr)=C(Cl)CH_2CH_3$	*E*	6.23 t	2.39 dt	1.03 t		
58866-49-2		*Z*	5.99 t	2.16 dt	1.03 t		
58866-50-5	$HC(SAr)=C(Cl)CH(CH_3)_2$	*E*	6.20 s	3.32 h′	1.08 d		
58866-51-6	$HC(SAr)=C(Cl)C(CH_3)_3$	*E*	6.24 s		1.34 s		
58866-52-7	$HC(SAr)=C(Cl)(CH_2)_2CH_3$	*E*	6.22 s	2.4 m	1.5 m	1.00 t	
58866-53-8	$HC(SAr)=C(Cl)(CH_2)_3CH_3$	*E*	6.23 s	2.4 m	1.6 m	1.4 m	0.98 t
	X = Cl; Y = SAr						
58866-54-9	$HC(Cl)=C(SAr)CH_3$	*E*	6.31 q	1.95 d			
58866-55-0		*Z*	6.04 q	1.73 d			
58866-56-1	$HC(Cl)=C(SAr)CH_2CH_3$	*E*	6.26 t	2.41 dt	1.01 t		
58866-57-2		*Z*	6.04 t	2.31 dt	1.02 t		
58866-58-3	$HC(Cl)=C(SAr)CH(CH_3)_2$	*E*	6.11 s	3.29 h′	1.03 d		
58866-59-4	$HC(Cl)=C(SAr)C(CH_3)_3$	*E*	6.37 s		1.30 s		
58866-60-7	$HC(Cl)=C(SAr)(CH_2)_2CH_3$	*E*	6.20 s	2.4 m	1.5 m	0.99 t	
58866-61-8	$HC(Cl)=C(SAr)(CH_2)_3CH_3$	*E*	6.18 s	2.4 m	1.5 m	1.5 m	0.97 t

possible products which can be formed by the addition of 4-chlorobenzenesulfenyl chloride to an unsymmetrical alkyne was obtained in the following manner. The NMR spectrum of the reaction mixture was taken immediately after mixing. The reaction mixture was irradiated to isomerize the *E* to the *Z* isomers and the NMR spectrum was again recorded. Hydrogen chloride was added to a fresh reaction mixture to catalyze the Markownikoff to anti-Markownikoff rearrangement.

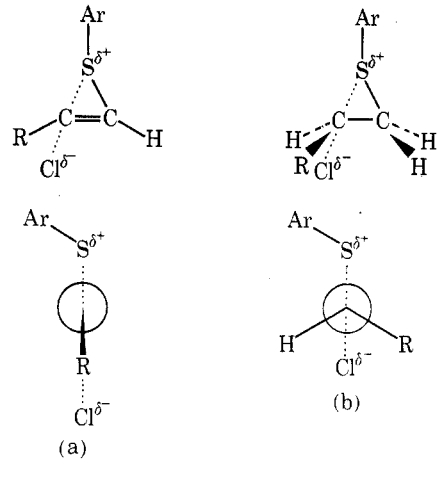
The assignment of peaks in the carbon-13 magnetic resonance spectrum for each regio- and stereoisomer is based upon two well-established relationships.[9] The carbon-13 chemical shifts of carbons attached to a carbon–carbon double bond appear at higher field for the *Z* than for the *E* isomer. Furthermore, the carbon-13 chemical shift for an olefinic carbon is at lower field when bonded to chlorine than to sulfur. Use of these two relationships permitted the assignments of the peaks of the adducts of unsymmetrical disubstituted and terminal alkynes in Tables IV and V, respectively.

Further confirmation of the product regio- and stereochemistry is obtained from their proton magnetic resonance spectra given in Tables VI and VII. The following relationships between adduct configuration and proton chemical shift have been previously observed.[10–13] In Table VI, (1) the chemical shift of protons vicinal to chlorine are observed at lower field relative to those vicinal to the arylthio group, (2) the chemical shifts of γ protons in the *Z* isomers are observed at higher field relative to those in the *E* isomer. These two observations serve to confirm the regio- and stereochemistry of the adducts formed by addition to the unsymmetrically disubstituted alkynes **9–11**.

The proton spectra are not as helpful in distinguishing between the isomers of the products of addition to the terminal alkynes. In Table VII, the same relationship exists between the chemical shifts of the γ protons and the *E* and *Z* configuration of the adducts. However, the position of the vinyl proton does not always follow the usual relationship between adjacent heteroatom electronegativity and chemical shift position. Fortunately, the carbon-13 spectra allow unambiguous determination of product regiochemistry.

The observation that the products of addition to terminal alkynes are predominantly those with anti-Markownikoff orientation clearly indicates that the alkyl groups exert a strong steric effect in the product-determining transition state. The effect of alkyl groups on product regiochemistry is generally more pronounced in the addition to alkynes than in the addition to similarily substituted alkenes.[1] Examination of the product-determining transition states for both reactions, illustrated in Chart I, provides an explanation. In the

Chart I



(a) (b)

product-determining transition state for addition to the alkynes (Chart Ia), the carbon of the substituent, the thiirenium ring, and the chloride ion all lie in the same plane. In contrast, the substituents on the thiiranium ion are above and below the plane containing the chloride ion and the thiiranium ring (Chart Ib). Consequently the steric hindrance between the entering chloride ion and the alkyl substituent is greater in the product-determining transition state for addition to alkynes than for ethylenes.

The regiochemistry of the products of addition to the unsymmetrically disubstituted alkynes is consistent with such steric control. Thus as the size of the substituent increases

from ethyl to isopropyl to *tert*-butyl, the amount of product with Markownikoff orientation decreases.

The addition to 4,4-dimethyl-2-pentyne forms small amounts of products with *Z*-Markownikoff and *Z*-anti-Markownikoff orientation. It is not yet clear if these products are the result of kinetic control or are the result of rapid isomerization of the major products of anti stereospecific addition.

Summary. The data presented clearly establish that alkyl groups have a different effect upon the rates than on the product composition of addition of 4-chlorobenzenesulfenyl chloride to alkynes. In the rate-determining transition state the effect of all of the alkyl groups, except *tert*-butyl, is predominantly polar. In the product-determining transition state, steric effects dominate.

Experimental Section

The alkynes were obtained commercially and their purity was verified by GLC and NMR.

4-Chlorobenzenesulfenyl chloride was prepared as previously described.[14]

1,1,2,2-Tetrachloroethane was purified as previously described.[14]

General Procedures. Ultraviolet Isomerization. A 2% solution of the *E* isomer, in benzene, was irradiated through Pyrex and copper sulfate filter for 40 h. The solvent was removed and the residue was dissolved in $CDCl_3$ and its proton and ^{13}C NMR spectrum recorded. The data are given in Tables IV–VII.

Acid-Catalyzed Isomerization. Anhydrous gaseous HCl was bubbled into a 1 M solution of the reaction mixture in benzene for approximately 1 min. Aliquots were taken from the solution, which was kept at room temperature. The solvent was removed, the residue was dissolved in $CDCl_3$, and its proton and ^{13}C NMR spectrum recorded. The data are given in Tables IV–VII. After several days the solutions began to darken and the NMR spectra indicated extensive decomposition.

Kinetics. Solutions for kinetic runs were prepared in general by direct weighing. The initial concentration of 4-chlorobenzenesulfenyl chloride was in the range $1 \pm 0.1 \times 10^{-3}$ M. The kinetic runs were carried out under pseudo-first-order conditions with a 20–80 times excess concentration of alkyne. When the alkyne was a gas at room temperature, the gas was bubbled into a given quantity of solvent and its concentration was determined by titration with a standard solution of 4-chlorobenzenesulfenyl chloride. The end point was taken as the appearance of the characteristic yellow of the slight excess of sulfenyl chloride. After the kinetic runs, the alkyne concentration was redetermined. No loss of alkyne by evaporation was ever detected.

All kinetic runs except for acetylene were carried out on a Durrum-Gibson stopped-flow spectrophotometer as previously described.[14] Rates of addition to acetylene were measured under pseudo-first-order conditions using the same concentrations of substrates as for the stopped-flow measurements, on a Cary 16 spectrophotometer with an external recorder by means of standard procedures.

Product Compositions. A solution of 0.12 g (0.001 mol) of 4-chlorobenzenesulfenyl chloride in 5 ml of 1,1,2,2-tetrachloroethane (TCE) was added dropwise to a solution containing 0.001 mol of alkyne in 3 ml of TCE at room temperature. The solvent was evaporated in a stream of dry nitrogen to constant weight. The residue, which corresponded to a quantitative yield, was dissolved in $CDCl_3$ and analyzed by NMR.

Analytical samples were prepared by adding a solution of 0.12 g (0.001 mol) of 4-chlorobenzenesulfenyl chloride in 5 ml of methylene chloride to 0.001 mol of alkyne in 3 ml of methylene chloride at room temperature. The solvent was evaporated in a stream of dry nitrogen to constant weight. Attempts to purify the residue by GLC or distillation led to decomposition. Satisfactory elemental analysis for **1–5, 8–10, 12** for C, H, Cl (±0.4%) were obtained directly upon removal of the solvent.

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Registry No.—4-Chlorobenzenesulfenyl chloride, 933-01-7; 1,1,2,2-tetrachloroethane, 630-20-6.

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Halogenated Ketenes. 29. Further Studies on Mixed Dimerizations[1]

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The mixed dimerizations of methylchloro- and *tert*-butylchloroketenes with methyl-*n*-propyl- and methylisopropylketenes resulted in equal amounts of the isomeric cyclobutanediones. *tert*-Butylketene codimerized with methylchloro-, methylbromo-, *tert*-butylchloro-, and *tert*-butylbromoketenes to yield only 2-oxetanone dimers. The β-keto acid chlorides prepared by the addition of α-chloropropionyl chloride and dichloroacetyl chloride to dimethylketene reacted with triethylamine to yield only the corresponding 2-oxetanones.

The dimerization of ketenes is regarded as a $[_\pi2_s + _\pi2_a]$ concerted process with a high negative entropy of activation and little solvent polarity dependence.[2] One of the ketene molecules participates as a $_\pi2_s$ component, while the other acts in a normal $_\pi2_a$ fashion, whereby the transition state involves an orthogonal approach of the reactant molecules.[3]

Dehmlow has recently reported that the thermal dimerization of some isolated unsymmetrical ketoketenes such as phenylmethyl-, benzylmethyl-, and benzylphenylketenes produced *cis*-cyclobutanediones. The same dimerization of benzylphenylketene by the dehydrochlorination of 2,3-diphenylpropanoyl chloride with either triethylamine or by heating above 230 °C produced both *cis*- and *trans*-cyclobutanediones. The proposed mechanism to produce the trans isomer was considered to be through the β-keto acid chloride, 2-benzyl-3-keto-2,4,5-triphenylpentanoyl chloride.[4]