Transmission of Substituent Effects across Both Double Bonds of Allenes. Rates and Products of Addition of Arenesulfenyl Chlorides to Allene and Its Methyl-Substituted Derivatives[1]

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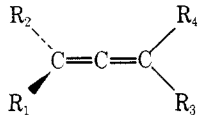
The rates and products of addition of benzenesulfenyl chloride in methylene chloride and 4-chlorobenzenesulfenyl chloride in 1,1,2,2-tetrachloroethane to allene and its five methyl-substituted derivatives have been determined. Substituting the hydrogens on allene by methyl groups has a large effect upon the rate of addition. The rates of addition to 2,3-pentadiene and 3-methyl-1,2-butadiene are almost identical, indicating that the effect of a methyl group is transmitted across both double bonds. Products are formed by addition to both double bonds. The mechanistic implication of these results is discussed.

The effect of substituents upon molecular properties has been a subject of continuing interest to chemists. Considerable effort has been made to learn how substituents affect the positions of equilibria and the rates of many chemical reactions. Most of what is known about the transmission of substituent effects from one part of a molecule to another has been obtained from studies on aromatic or simple aliphatic compounds. While the reactions of propadiene (allene) and its derivatives have been extensively studied,[3–5] little is known about the ability of the two double bonds in allene to transmit substituent effects. To study this problem, we have examined the effect of progressively substituting the hydrogens on allene by methyl groups on the rates and products of addition of arenesulfenyl chlorides. The results, reported in this paper, support the view that substituent effects are transmitted across both double bonds in electrophilic additions to allenes.

Results

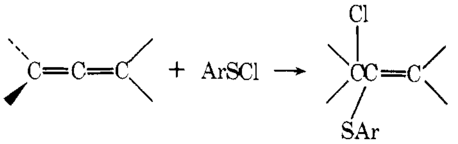
We have measured the rates of addition of benzenesulfenyl chloride (**1**) in methylene chloride and 4-chlorobenzenesulfenyl chloride (**2**) in 1,1,2,2-tetrachlorethane to allene (**3**) and its five methylated derivatives (**4–8**) at 25 °C by means of the stopped-flow technique using a Durrum–Gibson stopped-flow spectrophotometer. The rates of disappearance of **1** and **2** were followed by measuring the decrease in their absorptions at 392 nm. The additions were found to exhibit second-order kinetics, first order in both allene and arenesulfenyl chloride, to at least 80% completion of the reaction. The observed rate constants which are averages of at least three measurements are given in Table I.



3, $R_1 = H; R_2 = H; R_3 = H; R_4 = H$
4, $R_1 = H; R_2 = H; R_3 = H; R_4 = CH_3$
5, $R_1 = CH_3; R_2 = H; R_3 = CH_3; R_4 = H$
$R_1 = H; R_2 = CH_3; R_3 = H; R_4 = CH_3$
6, $R_1 = H; R_2 = H; R_3 = CH_3; R_4 = CH_3$
7, $R_1 = CH_3; R_2 = H; R_3 = CH_3; R_4 = CH_3$
8, $R_1 = CH_3; R_2 = CH_3; R_3 = CH_3; R_4 = CH_3$

The initially observed products of the addition of arenesulfenyl chlorides to allenes are 1:1 adducts. Their structures were determined by proton and carbon-13 magnetic resonance spectroscopy. The regiochemistry of the adducts was established from the chemical shifts of the protons and carbons α to chlorine. This assignment is based upon the observation that protons and carbons α to chlorine are deshielded relative to those α to sulfur.[7] The proton and carbon-13 data for the adducts and several model compounds are given in Tables II and III.

Several workers have reported that the addition of sulfenyl chlorides to allenes forms products in which the sulfur is bonded to the vinyl carbon (eq 1).[4,8,9] Our results are in agreement. Thus, the chemical shifts of the methylene protons of the product of the addition of benzenesulfenyl chloride to allene are similar to those of 2,3-dichloropropene. Furthermore the one-bond C–H coupling constant for the methylene carbon, 152.3 Hz, is in the range expected for a carbon directly bonded to a halogen: e.g., CH_3Cl, J = 148.6 Hz; CH_3Br, J = 150.05 Hz; CH_3I, J = 150.3 Hz. A smaller coupling constant would be expected for a carbon bonded to sulfur; e.g., $(CH_3)_2S$, J = 138 Hz.[10] Thus, the use of both proton and carbon-13 magnetic resonance spectroscopy establishes the structure of the adduct as **9**, in accord with the results of Mueller and Butler.[8] The regiochemistry of the other adducts can be established in a similar manner from the data in Tables II and III.



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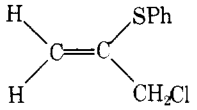

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The additions to **4**, **5**, and **7** form E and Z isomeric adducts whose structures were established by carbon-13 magnetic resonance spectroscopy. The assignments are based upon the well-established relationship that the carbon-13 chemical shifts of carbons bonded to a carbon–carbon double bond appear at higher field when the carbons are oriented cis to another functional group than when they are trans to it.[11]

After standing for several hours at 25 °C, the NMR spectrum of the product is observed to change in some cases. For propadiene (**3**), this change is due to formation of the diadduct. When E and Z isomers are formed as products, an increase in the amount of the Z isomer is observed at the expense of the E isomer. The formation of the diadduct can be explained by the well-established reversibility of the additions of arenesulfenyl chlorides to alkenes,[6] while the latter isomerization is due to an allylic rearrangement. These observations suggest that the product composition may change during the addition. We are unable to check this because the rates of addition are too fast. Consequently, we cannot establish conclusively that the observed products are those of kinetic control.

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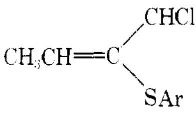
Table I. Second-Order Observed Rates of Addition of Arenesulfenyl Chlorides to a Series of Allenes at 25 °C

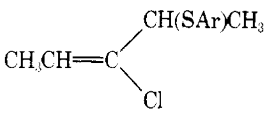
compd	benzenesulfenyl chloride in CH_2Cl_2		4-chlorobenzenesulfenyl chloride in TCE[a]	
	k_{obsd}, $M^{-1}\ s^{-1}$	k_{rel}	k_{obsd}, $M^{-1}\ s^{-1}$	k_{rel}
$CH_2{=}C{=}CH_2$ (**3**)	0.698	1.0	2.65	1.0
$CH_2{=}C{=}CHCH_3$ (**4**)	12.9	18.5	115	43
$CH_3CH{=}C{=}CHCH_3$ (**5**)	171	245	554	213
$CH_2{=}C{=}C(CH_3)_2$ (**6**)	159	230	512	193
$CH_3CH{=}C{=}C(CH_3)_2$ (**7**)	1039	1488	3760	1418
$(CH_3)_2C{=}C{=}C(CH_3)_2$ (**8**)	2360	3400	8605	3309

[a] TCE = 1,1,2,2-tetrachloroethane.

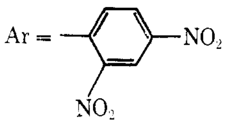
The percentage of each product was determined from the integrated area of nonoverlapping peaks in the proton spectrum (either 60 or 100 MHz) immediately after mixing. The initially observed product distribution for each allene is given in Table IV. These results are in agreement with previous results with one exception. Jacobs has reported that the addition of 2,4-dinitrobenzenesulfenyl chloride to **5** forms the two regioisomers **10** and **11**.[4a] We believe that the NMR data are better explained by a product composition consisting of a mixture of (*E*)- and (*Z*)-4-chloro-2-penten-3-yl phenyl sulfide (**12** and **13**, respectively). This conclusion is based upon the following facts. Firstly carbon and protons geminal or vicinal to chlorine are considably deshielded relative to sulfur.[7] Therefore, it would be surprising that the chemical shifts of the methyl groups bonded to the saturated carbon are nearly identical for the two isomers.[12] Similarly, the carbon-13 chemical shifts at δ 55.14 and 61.29 are in the region expected for such a carbon bonded to chlorine. If bonded to sulfur, its chemical shift would be at δ 45 based upon the carbon-13 spectra of the model compounds (*E*)-(2*RS*,5*RS*)- and (*E*)-(2*RS*,5*SR*)-5-chloro-3-hexen-2-yl 4′-chlorophenyl sulfide. Finally, the mass spectra of both **12** and **13** give rise to $M^+ - 63$ fragments (*m/e* 149) corresponding to the loss of C_2H_4Cl radicals. In neither case were ions observed at *m/e* 137, which would correspond to the loss of a $C_2H_4SC_6H_5$ fragment. Consequently, we conclude that the regiochemistries of **12** and **13** are identical and that they are *E* and *Z* isomers. A similar result has been observed in the methoxymercuration of **5**.[5a]

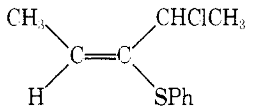

$CH_3CH{=}C(CHClCH_3)(SAr)$

10


$CH_3CH{=}C(CH(SAr)CH_3)(Cl)$

11





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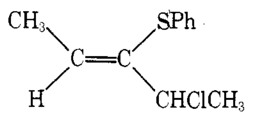

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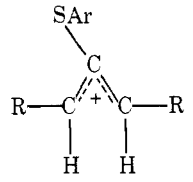
Discussion

From the rate data in Table I, it is clear that substituting the hydrogens on allene by methyl groups has a large effect on the observed rate of addition. The effect is almost multiplicative. A plot of log k_2 vs. the number of methyl groups shows a slight curvature, unlike a similar plot for ethylene which is linear.[13] Particularly interesting is the similarity of the observed rates of addition to **5** and **6** in the same solvent, indicating that the polar effect of a methyl group is not restricted to the double bond to which it is bonded.

Rearrangement of the allenes to either isomeric alkynes or dienes does not occur prior to addition. This is evident from the rates of addition to the allenes, which are all faster than the addition to isomeric alkynes[14] or dienes[15] under identical conditions.

Two mechanisms can be proposed to account for the observed effect of the methyl groups. One involves an allylic intermediate **14**, while the other involves a thiiranium ion (or ion pair) intermediate **15**[16,17] The former mechanism involves a rate-determining transition state that must resemble the intermediate ion **14**. Rate-determining formation of **14** directly from the allene requires bond rotation in the allene portion while bond formation occurs with the electrophile. Such a concerted process seems unlikely. Alternatively, it is possible that a sulfurane such as **16** may be formed first, which then undergoes a rate-determining ring opening. For the addition to unsymmetrical allenes, such a mechanism would involve at least two sulfuranes and consequently two or more competing paths.



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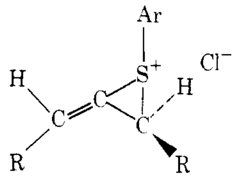

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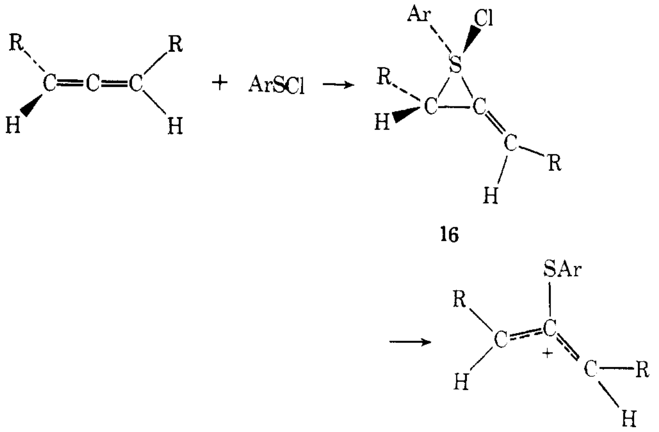


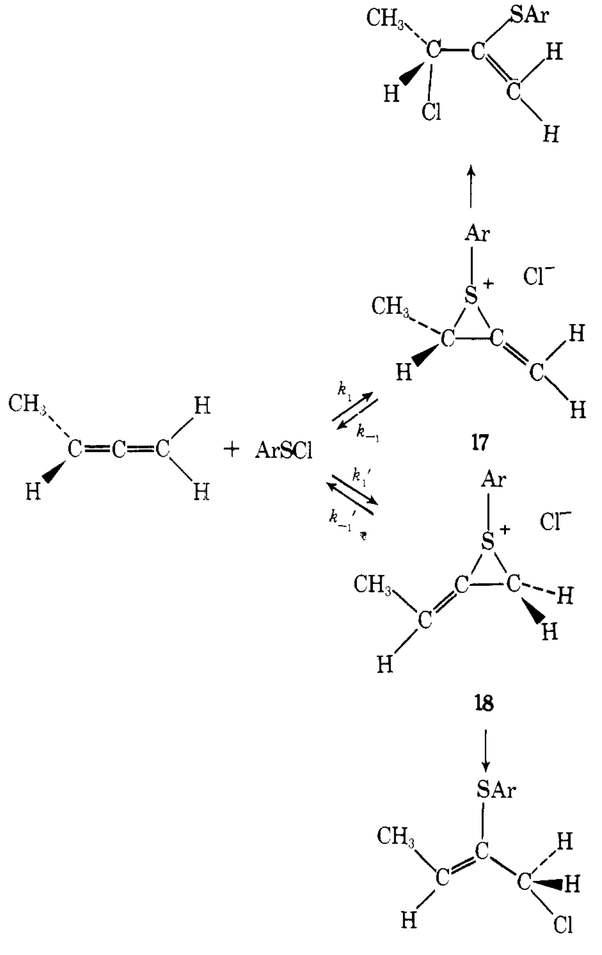
16

A bridged rate-determining transition state is in accord with the usual mechanism of electrophilic additions of arenesulfenyl chlorides to alkenes and alkynes.[18] For the addition to unsymmetrical allenes, such a mechanism would involve the formation of the two intermediates **17** and **18**. We cannot establish experimentally that the intermediates **17** and **18** are formed irreversibly. Therefore we cannot use the product composition to obtain the ratio k_1/k_1', and consequently we are limited to comparing observed rate constants. Despite this limitation, it is possible to compare the rates of addition of

Table V. Rates of Addition of 4-Chlorobenzenesulfenyl Chloride to a Series of Methyl-Substituted Ethylenes and Allenes in 1,1,2,2-Tetrachloroethane at 25 °C

allenes	k_{obsd} allenes, $M^{-1} s^{-1}$	k_2 ethylenes, $M^{-1} s^{-1}$	ethylenes[a]	no. of methyl groups
$CH_2{=}C{=}CH_2$ (3)	2.65	65.1	$CH_2{=}CH_2$	0
$CH_3CH{=}C{=}CH_2$ (4)	115	205	$CH_3CH{=}CH_2$	1
$(CH_3)_2C{=}C{=}CH_2$ (6)	512	551	$(CH_3)_2C{=}CH_2$	2
$CH_3CH{=}C{=}CHCH_3$ (5)	554	1340	$CH_3CH{=}CHCH_3$ (cis)	2
		434	$CH_3CH{=}CHCH_3$ (trans)	2
$(CH_3)_2C{=}C{=}CHCH_3$ (7)	3760	3030	$(CH_3)_2C{=}CHCH_3$	3
$(CH_3)_2C{=}C{=}C(CH_3)_2$ (8)	8605	7760	$(CH_3)_2C{=}C(CH_3)_2$	4

[a] Data from ref 13.



derivatives is 1:3.2:8.5, while the ratio for the allene derivatives is 1:210:3200.

Furthermore, from the data in Table V it is clear that except for allene, ethylene, and *cis*-2-butene the observed rates of addition are similar for ethylenes and allenes containing the same number of methyl groups. Such a result is surprising when compared to the difference in rates of addition to ethylene and allene. This means that the difference in transition state energies is larger than the difference in ground state energies on addition to ethylene vs. allene. In contrast, the difference in the ground state energies is about the same as the difference in the transition state energies for the addition to 2,3-pentadiene vs. *trans*-2-butene since their rates of addition are almost the same. Thus, the rate-determining transition state is stabilized equally well by a methyl as by an ethylidene ($=CHCH_3$) group. From the data, it seems that the isopropylidene ($=C(CH_3)_2$) group is as good as two methyl groups in stabilizing the rate-determining transition state.

Our data do not permit us to distinguish between the two mechanistic possibilities: one involving an allylic ion intermediate 14 and the other a thiiranium ion 15. However, the thiiranium ion (or ion pair) mechanism becomes slightly more attractive when the data of previous workers are considered. Caserio[5a] has reported that the bromination of (*R*)-(−)-2,3-pentadiene in CCl_4 or methanol occurs in a highly anti stereoselective manner. In general, the additions of arenesulfenyl chlorides to alkenes and alkynes occur with a higher degree of anti stereoselectivity than does bromination. Thus, it would be expected that the stereochemistry of the addition of 4-chlorobenzenesulfenyl chloride to (*R*)-(−)-2,3-pentadiene would be similar.

In support of this view, Jacobs found that the addition of 2,4-dinitrobenzenesulfenyl chloride to 2,2-dimethyl-3,4-hexadienol, of unspecified absolute configuration, yielded active 3-(2,4-dinitrophenylthio)-1,5,5-trimethyl-Δ^3-dihydropyran.[4c] Unfortunately, neither the optical purities nor the relative configurations of either the product or starting allene were determined. Consequently, it is impossible to establish the stereospecificity of the addition.

While we cannot conclusively establish the mechanism of this addition, it is clear from our data that the effects of substituents are readily transmitted across both double bonds of allene.

Experimental Section

Microanalyses were carried out by A. B. Gygli Microanalysis Laboratory, Toronto, Can. ^1H NMR spectra were obtained on a Varian T-60 or HA-100 spectrometer. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer using a 16K memory. Chloroform-*d* was used as an internal lock and reference. All spectra were referenced to tetramethylsilane as an internal standard.

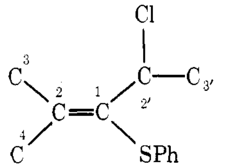
4-Chlorobenzenesulfenyl chloride was prepared as previously reported.[19] **Benzenesulfenyl chloride** was prepared by the method of Kharasch.[20] **1,1,2,2-Tetrachloroethane** was purified as previously reported.[19] **Methylene chloride** was purified as previously reported.[21] Kinetics and product compositions were carried out as previously described.[14]

Analytical samples were obtained by adding a solution of 0.14 g (0.001 mol) of benzenesulfenyl chloride in 5 mL of CH_2Cl_2 to 0.001 mol of diene in 3 mL of CH_3Cl_2 at room temperature. The solvent was evaporated in a stream of dry nitrogen to a constant weight. Attempts to purify the residue by GLC or distillation led to decomposition. Satisfactory elemental anlayses for C, H, and Cl (±0.4%) were obtained for the adducts of compounds 4 and 5 directly upon removal of the solvent. In each case the analytical samples were mixtures of isomers.

Propadiene, C.P. grade, was obtained from Matheson of Canada Ltd. **1,2-Butadiene, 2,3-pentadiene, and 3-methyl-1,2-butadiene** were obtained from Chemical Samples Co. **2-Methyl-2,3-pentadiene** was prepared by the method of Moore and Ward.[22] **2,4-Dimethyl-2,3-pentadiene** was a gift from Professor J. Powell of this department.

Acknowledgment. The continued financial assistance from the National Research Council of Canada is gratefully acknowledged. A University of Toronto Special Open Fellowship (1973–1974) and a National Research Council of Canada Postgraduate Scholarship (1974–1976) to D.G.G. and

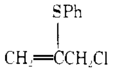
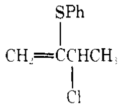
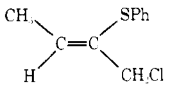
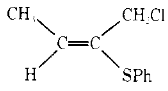
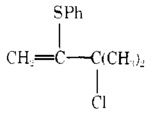
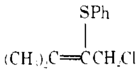
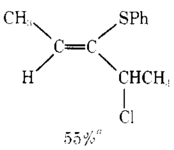
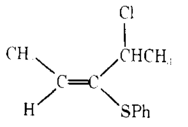
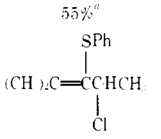
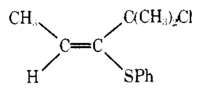
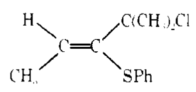
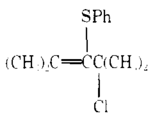
Table III. Observed Carbon-13 Magnetic Resonance Parameters for the Benzenesulfenyl Chloride Adducts



compd	chemical shifts, δ C_4	C_3	C_2	C_1	$C_{2'}$	$C_{3'}$	coupling constants, Hz $J_{C=CCH}$	$J^{cis}_{CC=CH}$	$J^{trans}_{CC=CH}$
$H_2C{=}C(SPh)CH_2Cl$			119.52	129.29	46.03		4.5	6.3	11.5
$H_2C{=}C(SPh)CHClCH_3$			116.82	146.89	58.47	24.83	4.2	4.8	11.3
$H_2C{=}C(SPh)C(CH_3)_2Cl$			113.61	152.48	70.40	32.66	4.5		
$CH_3CH{=}C(SPh)CH_2Cl$ (*Z*)	15.76		130.04	135.18	48.12			6.5	
$CH_3CH{=}C(SPh)CH_2Cl$ (*E*)		15.10	128.93	136.39	41.33				8.7
$(CH_3)_2C{=}C(SPh)CH_2Cl$	29.78	20.64	125.93	137.83	45.35				
$CH_3CH{=}C(SPh)CHClCH_3$ (*Z*)	15.81				61.29	24.75		4.2	
$CH_3CH{=}C(SPh)CHClCH_3$ (*E*)		14.84			55.14	23.83			11.7
$CH_3CH{=}C(SPh)C(CH_3)_2Cl$ (*Z*)	16.79				67.41	33.28		5.1	
$CH_3CH{=}C(SPh)C(CH_3)_2Cl$ (*E*)		14.99			62.53	33.12			12.3
$(CH_3)_2C{=}C(SPh)CHClCH_3$	29.99	21.36			65.52	25.02			
$\overset{3}{C}H_3\overset{2}{C}H(SAr)\overset{1}{C}H{=}\overset{2'}{C}HCH\text{-}Cl\underset{3'}{C}H_3$[a] (*E*)									
(2*RS*,5*RS*)		45.45	132.59	132.94	56.96	25.18			
(2*RS*,5*SR*)		45.30	132.41	132.70	56.82	25.09			

[a] Model compound.

Table IV. Products of the Addition of Benzenesulfenyl Chloride to Allene and Its Methyl-Substituted Derivatives

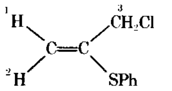
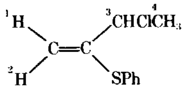
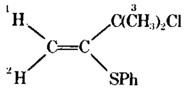
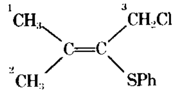
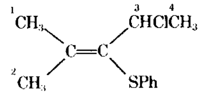
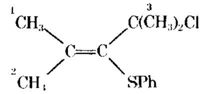
allene	products			
propadiene	 $CH_2{=}C(SPh)CH_2Cl$			
1,2-butadiene	 $CH_2{=}C(SPh)CHClCH_3$ 71%[a]	 20%[a]	 12%[a]	
3-methyl-1,2-butadiene	 $CH_2{=}C(SPh)C(CH_3)_2Cl$ 74%[a]	 $(CH_3)_2C{=}C(SPh)CH_2Cl$ 20%[a]	elimination products 6%	
2,3-pentadiene	 55%[a]	 45%[a]		
2-methyl-2,3-pentadiene	 $(CH_3)_2C{=}C(SPh)CHClCH_3$ 15%[a]	 32%[a]	 40%[a]	elimination products 13%
2,4-dimethyl-2,3-pentadiene	 $(CH_3)_2C{=}C(SPh)C(CH_3)_2Cl$ 25%	elimination products 75%		

[a] New compounds.

4-chlorobenzenesulfenyl chloride to methyl-substituted ethylenes and allenes. Such a comparison is made in Table V.

Evidence of transmission of substituent effects across both double bonds is found in the relative rates of addition to the symmetrical allenes. If both double bonds were completely independent of each other, it would be expected that the ratio of rates of addition to **3**, **5**, and **8** would parallel those of addition to ethylene, propene, and methylpropene. This is not the case. The ratio of the rates of addition to the ethylene

Table II. Observed Proton Magnetic Resonance Parameters for the Benzenesulfenyl Chloride Adducts

compd	registry no.	chemical shift assignments (CDCl$_3$),[a] δ				coupling constants, Hz						
		H$_1$	H$_2$	H$_3$	H$_4$	$J^{cis}_{HC=CCH}$	$J^{trans}_{HC=CCH}$	$J^{cis}_{HCC=CCH}$	$J^{trans}_{HCC=CCH}$	$^2J_{H_1H_2}$	$^3J_{H_1H_2}$	$^3J_{H_3H_4}$
	15893-06-8	5.63 dd	5.30 m	4.07 dd		0.9	≤0.4			≤0.4		
	67145-68-0	5.88 dd	5.13 d	4.58 qd	1.73 d	1.0	≤0.3			0.72		6.8
	67145-69-1	5.45 d	4.87 d	1.87 s						1.08		
${}^{1}CH_3\overset{2}{C}H{=}C(SPh)\overset{3}{C}H_2Cl$ (*Z*)	67145-70-4	1.93 dt	6.43 qt	4.07 q′		1.2			0.9		6.9	
${}^{1}CH_3\overset{2}{C}H{=}C(SPh)\overset{3}{C}H_2Cl$ (*E*)	67145-71-5	1.88 d	6.19 q	4.15 s			≤0.3	≤0.3			7.0	
	67145-72-6	1.90 s	1.93 t	4.50 q					1.0			
${}^{1}CH_3\overset{2}{C}H{=}C(SPh)\overset{3}{C}HCl\overset{4}{C}H_3$ (*Z*)	67145-73-7	1.83 dq	6.55 qd	4.80 qqd	1.61 d	0.5					7.25	7.00
${}^{1}CH_3\overset{2}{C}H{=}C(SPh)\overset{3}{C}HCl\overset{4}{C}H_3$ (*E*)	67145-74-8	1.82 d	5.95 q	5.15 q	1.60 d		≤0.4				6.75	6.60
${}^{1}CH_3\overset{2}{C}H{=}C(SPh)C(\overset{3}{C}H_3)_2Cl$ (*Z*)	67145-75-9	1.85 d	6.71 q	1.90 s							6.8	
${}^{1}CH_3\overset{2}{C}H{=}C(SPh)C(\overset{3}{C}H_3)_2Cl$ (*E*)	67145-76-0	1.82 d	6.03 q	1.90 s							6.9	
	67145-77-1	1.93 s	1.91 d	4.96 m	1.66 d				0.86			6.9
	67145-78-2	1.9 bs	1.9 bs	1.88 s								

[a] s = singlet, d = doublet, t = triplet, q = quartet, q′ = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, dqq = doublet of quartets of quartets, bs = broad singlet.

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Registry No.—**1**, 931-59-9; **2**, 933-01-7; **3**, 463-49-0; **4**, 590-19-2; **5**, 591-96-8; **6**, 598-25-4; **7**, 3043-33-2; **8**, 1000-87-9; (*E*)-(2*RS*,5*RS*)-5-chloro-3-hexen-2-yl 4′-chlorophenyl sulfide, 67145-79-3; (*E*)-(2*RS*,5*SR*)-5-chloro-3-hexen-2-yl 4′-chlorophenyl sulfide, 67145-80-6.

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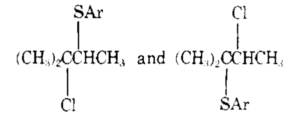

$$(CH_3)_2\overset{SAr}{C}\underset{Cl}{C}HCH_3 \text{ and } (CH_3)_2\overset{Cl}{C}\underset{SAr}{C}HCH_3$$

are δ 1.46 and 1.67, respectively.[13]

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9-Substituted Fluorenes. Evaluation of Substituent Effects via Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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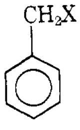
Received November 28, 1977

The carbon-13 NMR shielding effects for a series of 9-substituted fluorenes and 9-substituted 1-methylfluorenes, where the substituents are OH, Cl, Br, and I, have been determined. Shift data for several other fluorenyl systems are also presented. The substituent effects are discussed in terms of the transmission of electronic interactions. The substituent shifts at the meta and para carbon centers are analyzed using the Swain–Lupton parameters. Qualitatively, this analysis suggests that π-inductive effects are twice as important as hyperconjugative interactions. The first instances of downfield substituent shifts for γ-syn disposed carbons are observed, while upfield shifts are seen for the resonances of γ-anti carbons.

There has been considerable controversy concerning the transmission of the electronic properties of substituents to aromatic systems through potentially insulating centers such as in **1**.[2,3] Three types of substituent effects are generally considered to participate in systems like **1**: (1) σ-inductive effects; (2) π-inductive effects; and (3) resonance effects, in this case hyperconjugative interactions. Often the discussion of the mechanism for the transmission of the substituent effect is clouded by a lack of understanding or agreement of the terminology involved. So that this is not a problem here, the terms pertinent to the discussion (although available in the literature) will be reviewed.[2g,f,4]



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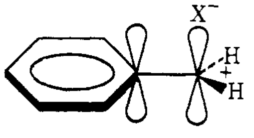
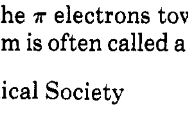
The *σ-inductive effect* requires a net charge transfer between the substituent and the σ framework, resulting in reorganization of the σ charge at various positions leading to *successive* polarization of the σ electrons. This interaction is most probably important only for the α and β carbons in these systems.[5]

Resonance effects result in a net transfer of charge between the aromatic π system and the substituent. In the context of the present discussion, hyperconjugation accounts for the resonance properties. Hyperconjugation requires specific stereochemical orientation and is most favorable when the dihedral angle of the potential hyperconjugative moiety is 0° with the aromatic π bonds.[6] This σ–π bond interaction is shown schematically below.



There are two mechanisms which fall under the heading of *π-inductive effects*:[2,4] (1) a process which causes reorganization of the aromatic π electrons by an *alternating* polarization of the π electrons,



(2) a polarization of the π electrons toward the ipso carbon. This second mechanism is often called a π-polarization effect.

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