

# A Non-Outer Sphere Mechanism for the Ionization of Aryl Vinyl Sulfides by Triarylamminium Salts

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**Abstract:** Evidence is presented that the formation of aryl vinyl sulfide cation radicals from the corresponding neutral precursors *via* reaction with tris(4-bromophenyl)aminium hexachloroantimonate in the context of a cation radical Diels–Alder addition to 1,3-cyclopentadiene does not occur *via* outer sphere electron transfer but by a mechanism involving strong covalent interaction between the aminium salt acting as an electrophile and the aryl vinyl sulfide substrate acting as a nucleophile.

The generation of cation radicals from corresponding neutral substrates has been accomplished by a variety of physical and chemical means, and the involvement of these cation radicals in efficient pericyclic chemistry has been confirmed and studied extensively.<sup>1</sup> The use of chemical agents, in particular triarylamminium salts, to generate cation radicals has proved to be especially convenient for synthetic purposes. Although many mechanistic aspects of the pericyclic reactions induced by aminium salts have been elucidated, relatively little is known concerning the specifics of the substrate ionization process *per se*. In particular, the fundamental question of the mechanism of these electron transfer (ET) reactions has received little attention.<sup>2</sup> Among the most plausible possibilities are (1) outer sphere ET, (2) inner sphere ET, and (3) a polar mechanism, that is actually a limiting form of the inner sphere ET mechanism. The latter involves the formation of a full covalent bond *via* electrophilic addition of the aminium salt to the substrate, to form a distonic cation radical, followed by homolysis of the newly formed covalent bond to yield the substrate cation radical and the neutral triarylamine (Scheme 1). The occurrence of nucleophilic attack on an aryl ring of a triarylamminium cation radical has already been well established,<sup>3</sup> but the possibility that such reactions could lead, *via* homolysis, to overall electron transfer has only recently received explicit consideration.<sup>4</sup> In a recent study of the ionization of stilbene by tris(4-bromophenyl)aminium hexachloroantimonate ( $\mathbf{1}^+$ ) in the context of a Diels–Alder addition to 2,3-dimethyl-1,3-butadiene, an outer sphere ET mechanism was suggested by substituent effect studies which reveal a transition state for ionization in which positive charge is distributed symmetrically over both aryl rings.<sup>4</sup>

## Results and Discussion

Extensive experimental and theoretical studies have previously established that substituent effects upon the ionization of meta- and para-substituted aryl vinyl sulfides and ethers in solution and in the gas phase preferentially correlate with the

Brown  $\sigma^+$  parameters as opposed to Hammett  $\sigma$  values (Scheme 2).<sup>5</sup> In sharp contrast, substituent effects upon the protonation of these same substrates at the carbon atom  $\beta$  to the heteroatom to yield an  $\alpha$ -heteroatom stabilized carbocation intermediate correlate preferentially with  $\sigma$  values. Further, substituent effects upon electrophilic reactions at the heteroatom of such substrates are expected to, and have been found to, correlate with  $\sigma$ .<sup>6</sup> Consequently a statistically validated preference for a correlation with  $\sigma$  represents strong evidence for an electrophilic reaction of these substrates, whereas a correlation with  $\sigma^+$  signals an electron transfer (ET) reaction producing a cation radical intermediate. The  $\sigma/\sigma^+$  criterion is therefore a useful diagnostic test for distinguishing outer sphere ET from electrophilic reactions of these two classes of electron rich substrates. Moreover, the utility of the  $\sigma/\sigma^+$  criterion can be significantly extended in instances where cation radical formation can be demonstrated by independent criteria. Specifically, the polar ET mechanism depicted in Scheme 1 is a stepwise process which involves initial electrophilic addition to the substrate. Providing that this step is rate determining, substituent effects should correlate with  $\sigma$  values. Consequently the  $\sigma/\sigma^+$  criterion can presumably be used to render the distinction between outer sphere ET and a polar ET mechanism. Further, an inner sphere ET mechanism which involves only a small to modest inner sphere interaction should presumably yield a much better correlation with  $\sigma^+$  than with  $\sigma$ , i.e., it should more closely resemble outer sphere ET than a polar reaction. The distinction between a stepwise polar ET mechanism and a concerted inner sphere ET mechanism which involves a very strong covalent interaction is more subtle but potentially can be accomplished *via* stereochemical studies (*vide infra*).

The reaction system studied in the present work is the Diels–Alder cycloaddition of aryl vinyl sulfides to 1,3-cyclopentadiene catalyzed by tris(4-bromophenyl)aminium hexachloroantimonate (Scheme 3). The aminium salt catalyzed Diels–Alder additions of phenyl vinyl sulfide to a variety of dienes have previously been confirmed, using several independent criteria, to occur *via* cation radical/neutral cycloaddition and specifically *via* addition of phenyl vinyl sulfide cation radicals to neutral diene molecules.<sup>7–9</sup> Carbocation mediated cycloadditions, in particular, have been decisively ruled out.<sup>10,11</sup> Several of the

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1997.

(1) Bauld, N. L. *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, 1992; Vol. 2, pp 1–66. Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307–5363.

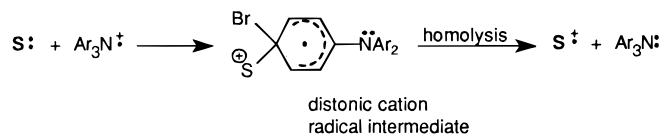
(2) Hubig, S. M.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 3842–3851.

(3) Eberson, L.; Olofsson, B.; Svensson, J.-O. *Acta Chem. Scand.* **1992**, *46*, 1005–1015.

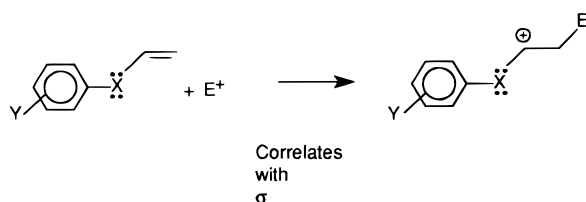
(4) Yueh, W.; Bauld, N. L. *J. Chem. Soc., Perkin Trans. 2* **1995**, 871–873; **1995**, 1715–1716.

(5) Bauld, N. L.; Aplin, J. T.; Yueh, W.; Endo, S.; Loving, A. *J. Phys. Org. Chem.* **1997**, in press.

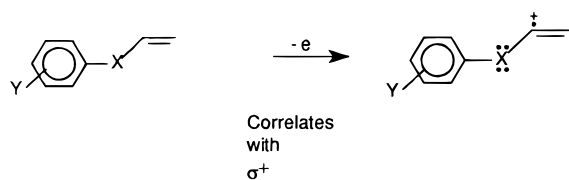
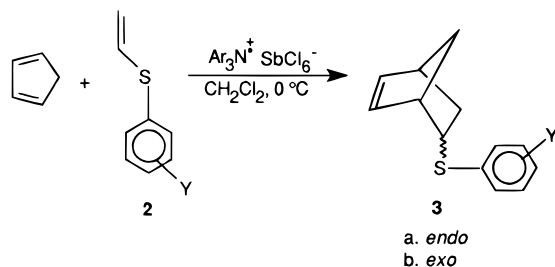
(6) Lewis, E. S.; Kukes, S.; Slater, C. D. *J. Am. Chem. Soc.* **1980**, *102*, 303–306. For example, reaction of aryl methyl sulfides with trimethylxonium fluoroborate yields  $r^2$  values of 0.993 and 0.902, respectively, for the  $\sigma$  and  $\sigma^+$  correlations.

**Scheme 1.** Mechanisms for the Formation of Cation Radicals in the Reactions of Neutral Substrates with Triarylammonium Salts**Outer Sphere (Concerted):** Negligible Covalent Bonding Between Reactants**Inner Sphere (Concerted):** Significant Covalency (Weak or Strong) Developed BetweenS: and  $Ar_3N^+$  in the Transition State**Polar (Stepwise):** Full Covalency Developed**Scheme 2.** The  $\sigma/\sigma^+$  Criterion for the Distinction between Electrophilic and Outer Sphere Electron Transfer Reactions of Aryl Vinyl Ethers and Sulfides

Electrophilic:



Outer Shell Electron Transfer:

X = O, S; Y = *m*- or *p*-substituent;  $E^+ = H^+$  or other electrophile**Scheme 3.** Diels–Alder Cycloadditions of Aryl Vinyl Sulfides to 1,3-Cyclopentadiene Catalyzed by Tris(4-bromophenyl)ammonium HexachloroantimonateAr = 4- $BrC_6H_4$ Y = 4-MeO; 4-Me; 3-Me; H; 4-Br; 3-Cl; 4- $CF_3$ , 3,5- $Cl_2$ 

previously developed mechanistic criteria have been applied to the specific reaction system under study in order more definitively to exclude a carbocation mediated cycloaddition mechanism. The inclusion of a hindered pyridine base in the reaction medium containing the ammonium salt is known to selectively suppress Brønsted acid catalyzed, carbocation mediated reactions. The reaction of Scheme 3, however, proceeds smoothly even in the presence of an excess of 2,6-di(*tert*-butyl)-4-methylpyridine. Further, added strong acid (triflic acid) fails to generate any of the Diels–Alder adducts when the ammonium

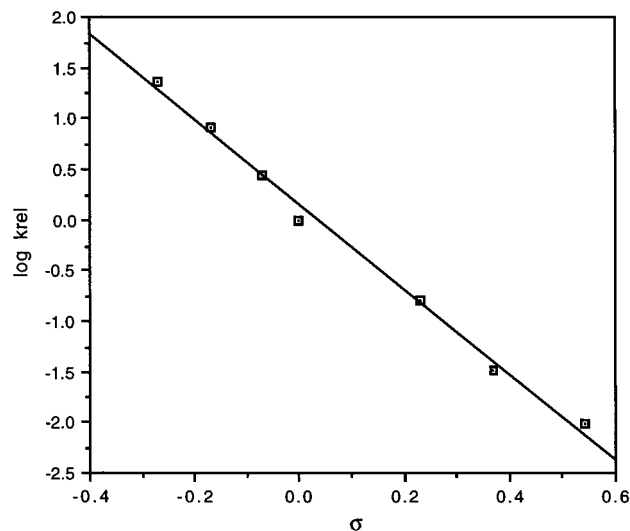
salt is omitted from the reaction medium. Finally, the same cycloadducts are formed in essentially the same diastereoisomeric (*endo:exo*) ratio when the reactions are carried out electrochemically (*via* anodic oxidation of the aryl vinyl sulfide) and by photosensitized electron transfer. The quantitative aspects of the electrochemical oxidations are especially significant and will be considered in greater detail in a subsequent section.

Cation radical Diels–Alder additions have been found to occur predominantly *via* dienophile cation radicals (aryl vinyl sulfide cation radicals in the present system) as opposed to diene cation radicals.<sup>1</sup> The evidence is especially clear in the case of cycloadditions involving aryl vinyl sulfides, where diene cation radicals have been found to produce vinylcyclobutane adducts preferentially.<sup>10</sup> The present reaction system was designed to further assure that the aryl vinyl sulfide component of the cycloaddition is the ionized component. The oxidation potential of 1,3-cyclopentadiene is *ca.* 0.4 eV higher than that of phenyl vinyl sulfide.<sup>12</sup> Further, this diene is essentially inert toward the ammonium salt in the absence of the aryl vinyl sulfide substrate. The cycloaddition step must therefore involve an ionized aryl vinyl sulfide molecule rather than an ionized diene molecule (Scheme 4).

**Products.** The reaction of phenyl vinyl sulfide with 1,3-cyclopentadiene in the presence of  $I^{+\cdot}$  in methylene chloride solvent at 0 °C cleanly yields the *endo* and *exo* Diels–Alder adducts **3a,b** in the ratio 3:1 (*endo:exo*). Only trace quantities of vinylcyclobutanes were observed, even at the earliest reaction times (low conversion). The *endo* and *exo* adducts were isolated and purified separately, and each was characterized by 2D <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and HRMS. The preference for the *endo* adduct is characteristic of cation radical Diels–Alder additions.<sup>1</sup>

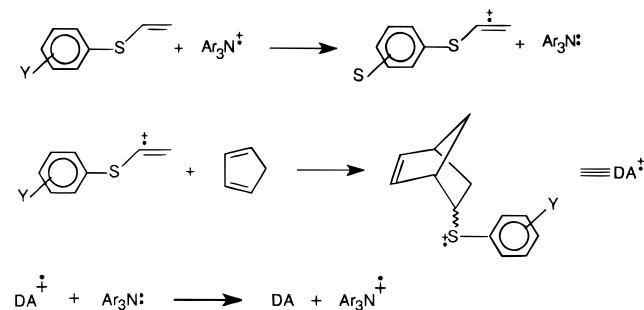
**Kinetics.** The relative rates of cycloaddition of eight aryl vinyl sulfides to 1,3-cyclopentadiene in dichloromethane solution were obtained by competition kinetics, using techniques which have previously been described (Table 1).<sup>13</sup> The plots of  $\log k/k_0$  vs  $\sigma$  and  $\sigma^+$  are given in Figures 1 and 2, respectively.

(7) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 5158–5159.(8) Harirchian, B.; Bauld, N. L. *Tetrahedron Lett.* **1987**, *28*, 927–930.(9) Harirchian, B.; Bauld, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 1826–1828.(10) Kim, T.; Pye, R. J.; Bauld, N. L., *J. Am. Chem. Soc.* **1987**, *112*, 6285–6290.(11) Reynolds, D. W.; Lorenz, K. T.; Chiou, H.-S.; Bellville, D. J.; Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1987**, *109*, 4960.(12) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993.



**Figure 1.** Hammett plot for the Diels–Alder cycloadditions of aryl vinyl sulfides to 1,3-cyclopentadiene, catalyzed by  $1^{+}$  in dichloromethane at 0 °C ( $\log k_{\text{rel}} = 0.20 - 4.26\sigma$ ;  $r^2 = 0.986$ ).

**Scheme 4.** Mechanism of the Cation Radical Diels–Alder Cycloaddition

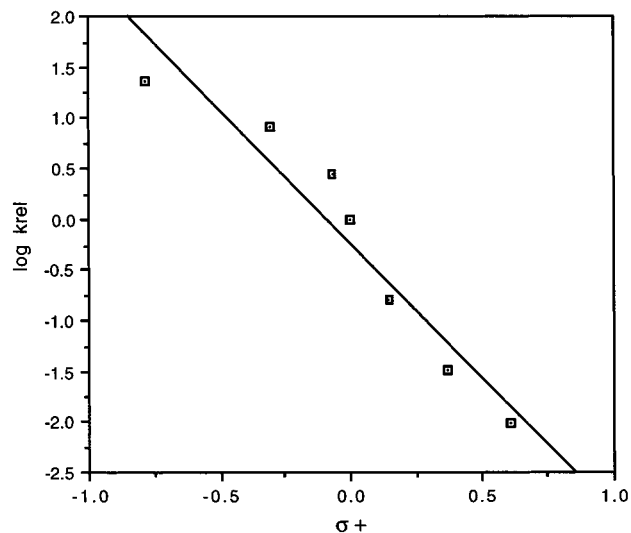


**Table 1.** Relative Rates of Diels–Alder Cycloadditions of Aryl Vinyl Sulfides to 1,3-Cyclopentadiene, Catalyzed by Tris(4-bromophenyl)ammonium Hexachloroantimonate

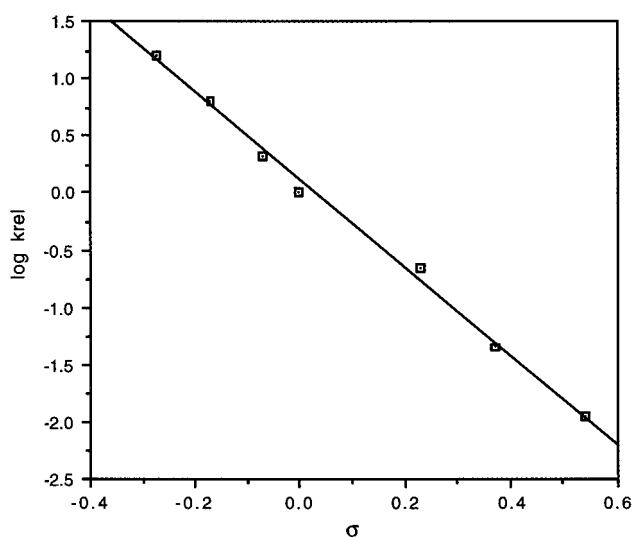
substituent	$\log k/k_0(\text{CH}_2\text{Cl}_2)$	$\log k/k_0(\text{CH}_3\text{CN})$
4-MeO	1.36	1.210
4-Me	0.922	0.815
3-Me	0.450	0.327
H	0.000	0.000
4-Br	-0.790	-0.652
3-Cl	-1.480	-1.340
4-CF <sub>3</sub>	-2.020	
3,5-Cl <sub>2</sub>		-1.95

The correlation with  $\sigma$  is seen to be excellent ( $r^2 = 0.986$ ), while that with  $\sigma^+$  is much worse ( $r^2 = 0.915$ ). Analogous kinetic studies were also carried out in the more polar solvent acetonitrile (Table 1). Again the plot of  $\log k/k_0$  vs  $\sigma$  (Figure 3,  $r^2 = 0.995$ ) is far superior to that vs  $\sigma^+$  (Figure 4,  $r^2 = 0.924$ ), and the statistical significance of the distinction is borne out by F tests for the data in both solvents.<sup>14</sup>

Although the preference for a  $\sigma$  over a  $\sigma^+$  correlation is maintained when the data point for the 4-methoxy derivative is omitted, it is noteworthy that the obtention of a *statistically significant preference* for the  $\sigma$  correlation critically depends upon the inclusion of this data point for all of the data sets reported in the paper. Consequently we have paid especially careful attention to this data point. Four independent measure-



**Figure 2.** Hammett–Brown plot for the Diels–Alder cycloadditions of aryl vinyl sulfides to 1,3-cyclopentadiene, catalyzed by  $1^{+}$  in dichloromethane at 0 °C ( $\log k_{\text{rel}} = -0.20 - 2.68\sigma^+$ ;  $r^2 = 0.915$ ).

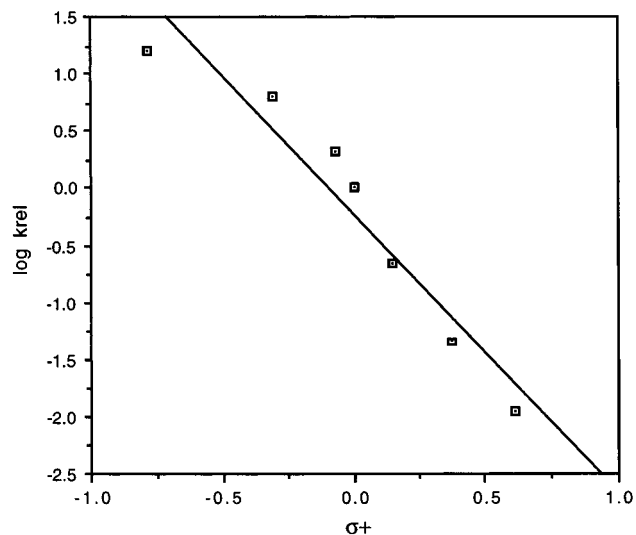


**Figure 3.** Hammett plot for the Diels–Alder cycloadditions of aryl vinyl sulfides to 1,3-cyclopentadiene, catalyzed by  $1^{+}$  in acetonitrile at 0 °C ( $\log k_{\text{rel}} = 0.12 - 3.85\sigma$ ;  $r^2 = 0.995$ ).

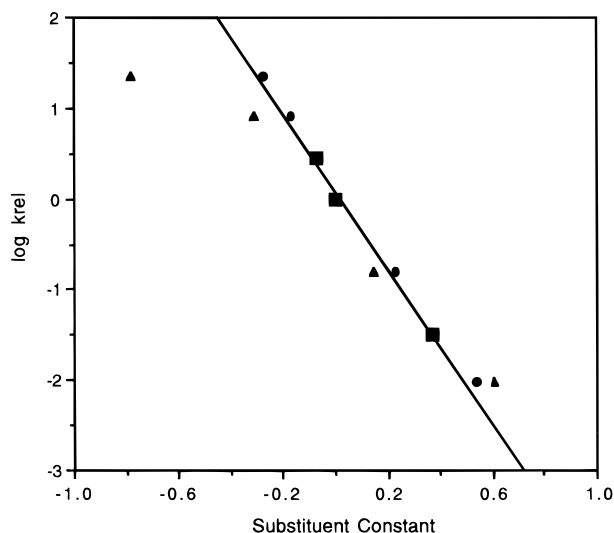
ments of the relative rate data for the competition between the 4-MeO and 4-Me derivatives have yielded the value  $2.73 \pm 0.06$ . For comparison, the predicted value for  $k(4\text{-MeO})/k(4\text{-Me})$  in a  $\sigma^+$  correlation, assuming a value of  $\rho$  determined by omitting the 4-MeO data point, is *ca.* 40! Importantly, the mass balance in these reactions (i.e., the percent of the reactions accounted for as either Diels–Alder adducts or recovered starting material) is quite high—in some cases as high as 99% (see Experimental Section). Consequently, the possibility that most of the cation radicals of the 4-MeOAVS substrate are lost *via* side reactions is negated. Further, the four independent measurements span a 25-fold range of relative cyclopentadiene: aryl vinyl sulfide concentrations (0.2–5), thus ruling out the possibility that the ionization step becomes reversible for this substrate. Note that absolute reaction rate measurements have confirmed that ionization is rate determining for the 4-Me derivative. Consequently, ionization must also be rate determining for the 4-MeO derivative. The foregoing discussion generates substantial confidence in the experimental value of the relative rate constant for the 4-MeOAVS, and, importantly, it also establishes that this substrate is not mechanistically abnormal. Confidence in the significance of the distinction

(13) Baltes, H.; Steckhan, E.; Schäfer, H. J. *Chem. Ber.* **1978**, *111*, 1294–1314. The peak potential for cyclopentadiene (*vs* Ag/AgCl) is given as 1.50 V. The peak potential for phenyl vinyl sulfide is 1.1 V.

(14) Yueh, W.; Bauld, N. L. *J. Phys. Org. Chem.* **1996**, *9*, 529–538.



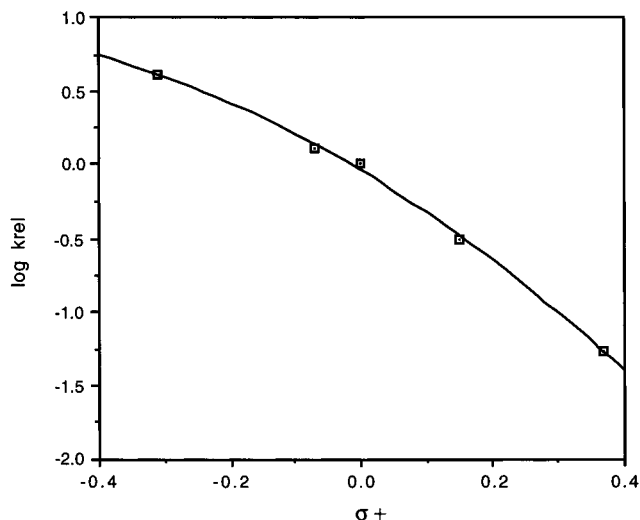
**Figure 4.** Hammett–Brown plot for the Diels–Alder cycloadditions of aryl vinyl sulfides to 1,3-cyclopentadiene, catalyzed by  $I^{*+}$  in acetonitrile at 0 °C ( $\log k_{\text{rel}} = -0.24 - 2.42\sigma^+$ ;  $r^2 = 0.924$ ).



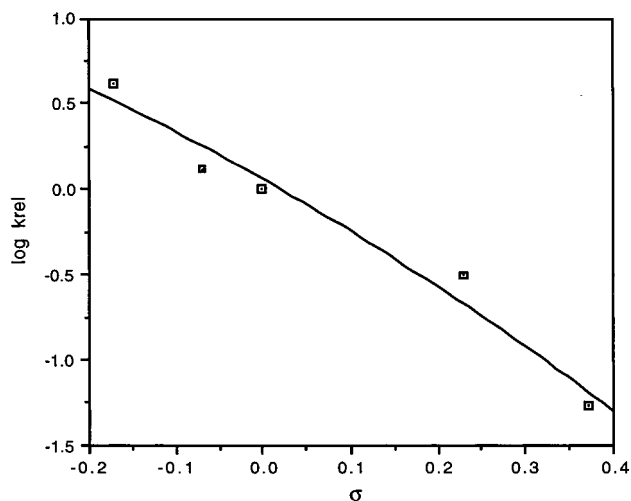
**Figure 5.** Hammett plot for the Diels–Alder cycloadditions of aryl vinyl sulfides to 1,3-cyclopentadiene catalyzed by  $I^{*+}$  in dichloromethane at 0 °C. The line shown is for the regression analysis of the meta points represented as squares ( $\rho = 4.28$ ,  $r^2 = 0.994$ ). The data for the para substituents is plotted both using  $\sigma$  values (circles) and  $\sigma^+$  values (triangles).

between the  $\log k_{\text{rel}}$  vs  $\sigma$  and  $\sigma^+$  correlations is provided by statistical tests (F-tests) which indicate the distinction is significant at or above the 95% confidence level. This point is brought home visually in an especially clear way in Figure 5, where only the points for meta substituted derivatives (for which  $\sigma$  and  $\sigma^+$  are equal) are used to determine the trend line. In the correlation with  $\sigma$  values (circles) the points for the para derivatives are all observed to fall very close to this line. However, in the correlation vs  $\sigma^+$  (triangles), *p*-MeO, *p*-Me, and *p*-Cl are all observed to deviate negatively from the line defined by the meta points. The deviation is greatest for 4-MeO, as it should be, but it is substantial for both 4-Me and 4-Cl. Finally, *p*-CF<sub>3</sub> deviates in a positive sense, as it should because its  $\sigma^+$  value is more positive than its  $\sigma$  value.

Clearly, the step which determines which aryl vinyl sulfide is preferentially ionized to the cation radical does not, in fact, resemble an aryl vinyl sulfide cation radical. Further, the  $\rho$  values observed ( $-4.21$  in dichloromethane;  $-3.85$  in acetonitrile) are much too large to be consistent with a very early



**Figure 6.** Hammett–Brown plot for the Diels–Alder cycloadditions of aryl vinyl sulfides to 1,3-cyclopentadiene in acetonitrile under electrochemical conditions ( $\log k_{\text{rel}} = -0.04 - 2.67\sigma^+ - 1.82(\sigma^+)^2$ ;  $r^2 = 0.999$ ).

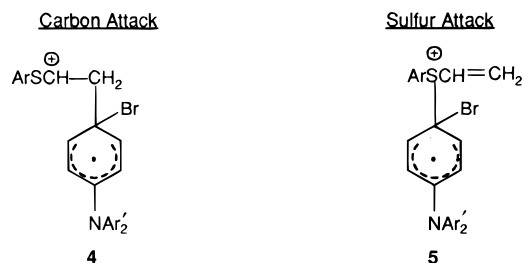


**Figure 7.** Hammett plot for the Diels–Alder cycloadditions of aryl vinyl sulfides to 1,3-cyclopentadiene in acetonitrile under electrochemical conditions ( $\log k_{\text{rel}} = 0.06 - 2.87\sigma - 1.33(\sigma)^2$ ;  $r^2 = 0.966$ ).

transition state resembling a loose complex. For comparison, the  $\rho$  value for the equilibrium formation of these same aryl vinyl sulfide cation radicals in acetonitrile was found to be  $-5.8$ . On the other hand,  $\rho$  values for electrophilic additions to phenyl vinyl sulfide have been found to be in the range  $-1.78$  to  $-3.0$ .<sup>15,16</sup> Consequently an outer sphere mechanism for ionization can be decisively ruled out. An inner sphere mechanism involving only a weak covalent interaction would appear to be similarly excluded. The data, however, are nicely consistent with an initial electrophilic step, involving reaction of the aminium salt electrophile either at the unsubstituted vinyl carbon or at the nucleophilic sulfur atom (Scheme 5) or with a concerted inner sphere mechanism involving very strong covalent interaction between the two reactants. Further insights into the specifics of the mechanism are provided by stereochemical data to be discussed in a subsequent section. That the ionization stage rather than the cycloaddition stage is rate determining is strongly indicated by several lines of evidence. First, the value of  $\rho$  is substantially smaller than the  $\rho$  value for the equilibrium

(15) Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*; McGraw-Hill: New York, 1989; pp 811–820.

(16) McClelland, R. A. *Can. J. Chem.* **1977**, *55*, 548–551.

**Scheme 5.** Two Potential Modes of Electrophilic Addition of Triarylammonium Ions to Aryl Vinyl Sulfides

ionization. In the case where ionization is reversible and cycloaddition is rate determining, the  $\rho$  value is considered likely to be much closer to the equilibrium  $\rho$  value. In one such case, the kinetic  $\rho$  value was found to be 83% of the equilibrium  $\rho$  value.<sup>17</sup> Secondly, added neutral triarylamine (**1**) is found not to retard the absolute rate of the cycloaddition. If ionization were reversible, the triarylamine should sharply depress the rate.<sup>18</sup> Finally, a doubling of the concentration of the diene leaves the absolute reaction rate essentially unchanged.<sup>19</sup>

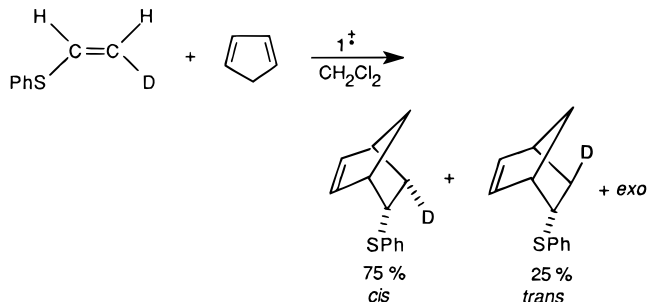
**The Reaction under Photochemical Electron Transfer Conditions.** Photosensitized electron transfer is a well established method for generating cation radicals and studying their cycloadditions to neutral molecules.<sup>10</sup> Acid is not generated under these conditions, and electron transfer is of the outer sphere type. When the subject reaction is studied using 1,4-dicyanobenzene as the sensitizer and the singlet excited state of this molecule is the single electron acceptor, the same Diels–Alder cycloadducts (**3a,b**) are formed cleanly, and the *endo*:*exo* ratio (2.9:1) is virtually identical to that found in the aminium salt catalyzed reaction. This result provides strong independent support for interpreting the latter reaction as a cation radical/neutral cycloaddition.

**The Reaction under Electrochemical Oxidation Conditions.** Anodic oxidation provides still another means of generating substrate cation radicals and studying their cycloadditions.<sup>20</sup> Using a reticulated vitreous carbon anode and acetonitrile as the solvent, phenyl vinyl sulfide again adds cleanly to 1,3-cyclopentadiene to yield **3a** and **3b**, with an *endo*:*exo* ratio quite similar (2.2:1) to those observed in the chemically and photochemically promoted reactions. By carrying these EC oxidations out at a voltage (1.05 V) equal to the oxidation potential of **1**, it was possible to provide oxidizing power comparable to that of **1**<sup>+</sup>. Since this voltage is less than the peak potential of phenyl vinyl sulfide (1.4 *vs* SCE) and grossly less than that of 1,3-cyclopentadiene (1.8 *vs* SCE), it can be confidently assumed that essentially only phenyl vinyl sulfide cation radicals are generated and give rise to the observed adducts.

**Kinetics under EC Conditions.** Electrochemical oxidations, particularly those carried out at a chemically relatively inert anode such as reticulated vitreous carbon, would appear highly likely to occur *via* an outer sphere mechanism, as opposed to an electrophilic, inner shell process. Given the extremely rapid rates of cycloaddition of cation radicals of substrates which have an unsubstituted vinyl moiety, it appeared possible that cycloadditions might, under at least some conditions, occur at a

**Table 2.** Relative Rates of Diels–Alder Cycloadditions of Aryl Vinyl Sulfides to 1,3-Cyclopentadiene under Electrochemical Oxidation Conditions

substituent	log $k/k_0$	substituent	log $k/k_0$
4-Me	0.614	4-Br	-0.501
3-Me	0.120	3-Cl	-1.27
H	0.000		

**Scheme 6.** The Reaction of Phenyl *cis*-2-Deuteriovinyl Sulfide with 1,3-Cyclopentadiene

rate competitive with or faster than back electron transfer from the anode and thus that anodic oxidation might provide for a kinetically controlled oxidation step in the subject Diels–Alder reactions under EC conditions. If these assumptions are valid, competition kinetic studies under anodic oxidation conditions could provide a contrasting example of outer sphere electron transfer, which should lead to a correlation of log  $k/k_0$  with  $\sigma^+$ . The kinetic data are contained in Table 2, and the plots of log  $k/k_0$  *vs*  $\sigma$  and  $\sigma^+$  are illustrated in Figures 6 and 7 (*vs*  $\sigma^+$  and  $\sigma$ , respectively). It is noted that both plots exhibit curvature. Analogous curvature has been observed in aminium salt catalyzed cycloadditions where the ionization step is shifting from kinetic to equilibrium control.<sup>17</sup> Significantly, a quadratic correlation of log  $k/k_0$  *vs*  $\sigma^+$  is of excellent quality ( $r^2 = 0.999$ ), while the similar plot *vs*  $\sigma$  is of lower quality ( $r^2 = 0.976$ ). These data are at least consistent with the scenario in which, to the extent that oxidation is kinetically controlled, the mechanism is of the outer sphere type.

**Stereochemistry.** Stereochemical studies appear to provide further insight into the specifics of the ionization process. Phenyl *cis*-2-deuteriovinyl sulfide was the substrate selected for these studies (Scheme 6).<sup>21</sup> When the reaction as catalyzed by **1**<sup>+</sup> was carried out, using the stereospecifically deuterium labeled substrate, the *endo* Diels–Alder adduct **3a** was isolated and found to be formed with 50% suprafacial stereospecificity and 50% stereorandomization (corresponding to 75% of the *cis,endo* adduct and 25% of the *trans,endo* adduct). The recovered substrate, however, was nearly completely stereorandomized (55% *cis*, 45% *trans*). These results suggest that the stereospecificity of the reaction is actually much higher than 50%, since the *trans*-deuterio substrate should be roughly equally as reactive as the *cis*-compound, and some of the *trans*-deuterio **3a** must have arisen from this isomer. The existence of even 50% of a stereospecific component would be surprising if ionization proceeds exclusively *via* electrophilic attack at carbon, since the most reasonable expectation is that torsional equilibration in intermediate **4** (Scheme 5) should be very fast compared to homolytic dissociation. However, electrophilic attack on sulfur to yield the vinylsulfonium ion **5** appears to provide a plausible path for the stereospecific formation of the phenyl *cis*-2-deuteriovinyl sulfide cation radical. Ample precedent for a stereospecific Diels–Alder addition step is avail-

(17) Hojo, M.; Masuda, R.; Kamitori, Y.; Okada, E. *J. Org. Chem.* **1991**, *56*, 1975–1976.

(18) Yueh, W.; Bauld, N. L. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1761–1766.

(19) This is a consequence of the formation of neutral **1** as a product of the ionization reaction: Lorenz, K. T.; Bauld, N. L. *J. Am. Chem. Soc.* **1987**, *109*, 1157–1160.

(20) This was verified for three different aryl vinyl sulfides (see Experimental Section).<sup>17</sup>

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able.<sup>22</sup> A concerted inner sphere mechanism for the electron transfer reaction is also tenable providing that the transition state closely resembles **4** or **5**, i.e., that a very strong covalent interaction (polar in character) is developed. This possibility is regarded as somewhat improbable, since it requires that a transition state very closely resembling **4** or **5** does not actually proceed to the full fledged intermediate. The mechanism for the isomerization of the starting material is presently unknown.

The discovery that the mechanisms of ionization of stilbenes and aryl vinyl sulfides by the aminium salt are quite different is not at all surprising. Steric effects which would adversely affect strong covalent attachment are much more severe in stilbene than in a vinyl sulfide. Further, concerted ionization of stilbene takes advantage of the conjugative effect of both aryl rings, whereas an electrophilic mechanism effectively utilizes only a single aryl ring. Finally, the presence of a nucleophilic sulfur atom is considered to sharply enhance the likelihood of an electrophilic attachment to aryl vinyl sulfides. It should prove to be of considerable interest to determine ionization mechanisms for a range of systems and to elucidate the effects of structure variation upon the mechanism of ionization.

## Conclusions

Substituent effect studies of the electron transfer reactions between aryl vinyl sulfide substrates and tris(4-bromophenyl)-aminium hexachloroantimonate decisively rule out both an outer sphere ET mechanism and an inner sphere mechanism which involves only a small to moderate covalent interaction between the aminium salt and the substrate. The preferred mechanism involves rate determining electrophilic attack on the substrate, followed by homolysis to the substrate cation radical, i.e., a *stepwise polar mechanism for ET*.

Stereochemical studies indicate sulfur is a more likely site of the electrophilic attack than the beta vinyl carbon. A concerted inner sphere mechanism having a *very strong* (polar) covalent interaction is also compatible with the kinetic and stereochemical data but is considered somewhat less likely on theoretical grounds.

## Experimental Section

**Analysis.** Analytic gas chromatographic (GC) analyses were performed on a Perkin-Elmer Model 8500 using a PE Nelson Model 1020 reporting integrator for data collection or a Varian Model 3700 using an HP 3390A integrator for data collection. Both instruments were equipped with flame ionization detectors and DB-1 capillary columns (J&W Scientific, 30 m × 0.25 mm on the PE and 15 M × 0.25 mm on the Varian with film thickness of 1 mm), using helium as the carrier gas. Naphthalene was used as internal standard for all the quantitative analyses. In the aryl vinyl sulfide (AVS) series the difference in response factors for phenyl vinyl sulfide and its cross adduct with 1,3-cyclopentadiene was small, and this was assumed to be the case for the entire series. The response factors calculated for the substituted aryl vinyl sulfides were therefore used for the respective cross adducts. Electrochemical measurements were performed using a BAS 100 electrochemical analyzer in the differential pulse voltammetry (DPV) mode scanning in the range of 500 to 1900 mV at a scan rate of 4 mV/s with a pulse amplitude of 50 mV, a pulse width of 50 ms, a pulse period of 1000 ms, and a sensitivity of  $1 \times 10^{-6}$ . The  $E_p^{ox}$  measurements *vs* Ag/Ag<sup>+</sup> were converted to *vs* SCE by adding 0.3 V to each value.

**Reagents.** The substituted aryl vinyl sulfides were prepared by modification of a literature procedure<sup>23</sup> with the exception of phenyl vinyl sulfide (Aldrich) and 4-bromophenyl vinyl sulfide.<sup>23</sup> Cylo-

pentadiene ( $E_p^{ox}$  1.8 V) was freshly prepared from dicyclopentadiene, stored at -20 °C, and used within 8 h.

**General Procedure for the Synthesis of Substituted Aryl Vinyl Sulfides (2).** An aryl Grignard reagent, from the reaction of an aryl bromide or iodide and excess Mg (concentration ~ 1 M), was added, *via* cannula, to a solution of 2-chloroethyl thiocyanate<sup>24</sup> in THF at 0 °C. After the addition was complete, the reaction was allowed to stir at room temperature for 1 h, at which time the reaction was cooled back to 0 °C, and a suspension of KOtBu (4- to 6-fold excess) in THF was carefully added. The reaction was refluxed for 1–2 h and checked by GC. If GC analysis indicated that the reaction was not complete, then ~2 more equiv of KOtBu were added, and reflux continued for another hour. The reaction was cooled to room temperature and then transferred to a separatory funnel containing 100 mL of 10% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 100 mL of saturated NaCl, and 200 mL of pentane. The aqueous layer was removed, and the organic layer was washed with 100 mL of saturated NaCl. The organic layer was then dried over MgSO<sub>4</sub>, and the solvent removed at reduced pressure on a rotary evaporator. The residue was vacuum distilled at ~5 Torr, allowing a small forerun of material before collecting the product. Yields are reported for isolated material of suitable purity (>95% by GC) for quantitative experiments. In some cases, multiple distillations were necessary to meet this requirement.

**4-Methoxyphenyl Vinyl Sulfide (4-MeO).** Using the above procedure, the Grignard reagent from 4-bromoanisole (18.7 g) and Mg (3.0 g) was added to 8.20 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 25 g of KOtBu in 100 mL of THF. Distillation gave 6.621 g (59.1%) of product determined to be >98% pure by GC: bp 115–120 °C at 5 Torr, <sup>1</sup>H NMR δ 3.76 (s, 3H), 5.1 (m, 2H), 6.43 (dd, 1H), 6.85 (d, 2H), 7.31 (d, 2H); <sup>13</sup>C NMR δ 55.1, 112.4, 114.7, 123.3, 133.5, 133.9, 159.5; LRMS *m/e* 166 (M<sup>+</sup>), 151 (base), 135, 121, 107, 77; HRMS *m/e* calcd for C<sub>9</sub>H<sub>10</sub>OS 166.0452; found 166.0453;  $E_p^{ox}$  1.097 V.

**4-Methylphenyl Vinyl Sulfide (4-Me).** Using the above procedure, 100 mL of a 1 M solution of 4-methylphenyl magnesium bromide (Aldrich) in diethyl ether was added to 8.10 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 15.4 g of KOtBu in 50 mL of THF and required additional KOtBu (10 g). Distillation gave 5.39 g (53.9%) of product determined to be >97% pure by GC: bp 95–105 °C at 5 Torr, <sup>1</sup>H NMR δ 2.3 (s, 3H), 5.2 (m, 2H), 6.45 (dd, 1H), 7.07 (d, 2H), 7.25 (d, 2H); <sup>13</sup>C NMR δ 21, 114.1, 129.8, 130, 131.2, 132.6, 137.3; LRMS *m/e* 150 (M<sup>+</sup>), 135 (base), 105, 91, 77; HRMS *m/e* calcd for C<sub>9</sub>H<sub>10</sub>S 150.0503; found 150.0498;  $E_p^{ox}$  1.267 V.

**4-Phenylphenyl Vinyl Sulfide (4-Ph).** Using the above procedure, the Grignard reagent from 4-bromobiphenyl (18.567 g), and Mg (2.198 g) was added to 9.68 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 35 g of KOtBu in 100 mL of THF and required additional KOtBu (10 g). Flash chromatography on silica with hexane and recrystallization from hexane afforded 4.72 g (28%) of product determined to be >97% pure by GC: mp 53–55 °C, <sup>1</sup>H NMR δ 5.36 (m, 2H), 6.5 (dd, 1H), 7.37 (m, 5H), 7.56 (m, 4H); <sup>13</sup>C NMR δ 115.7, 126.9, 127.4, 127.7, 128.8, 130.7, 131.7, 133.3, 140; LRMS *m/e* 212 (M<sup>+</sup>, base), 197, 185, 176, 167, 152, 135, 115, 77; HRMS *m/e* calcd for C<sub>14</sub>H<sub>12</sub>S 212.0656; found 212.0651;  $E_p^{ox}$  1.249 V.

**3-Methylphenyl Vinyl Sulfide (3-Me).** Using the above procedure, the Grignard reagent from 3-bromotoluene (17.122 g) and Mg (4.0 g) was added to 8.10 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 25 g of KOtBu in 70 mL of THF. Distillation gave 10.864 g (72%) of product determined to be >98% pure by GC: bp 93–94 °C at 5 Torr, <sup>1</sup>H NMR δ 2.32 (s, 3H), 5.3 (m, 2H), 6.5 (dd, 1H), 7.0 (m, 1H), 7.16 (m, 3H); <sup>13</sup>C NMR δ 21.2, 115.2, 127.4, 127.9, 128.9, 131, 132, 133.9, 138.9; LRMS *m/e* 150 (M<sup>+</sup>), 135 (base), 105, 91, 77; HRMS *m/e* calcd for C<sub>9</sub>H<sub>10</sub>S 150.0503; found 150.0497;  $E_p^{ox}$  1.312 V.

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**4-Chlorophenyl Vinyl Sulfide (4-Cl).** Using the above procedure, the Grignard reagent from 4-chloriodobenzene (9.65 g) and Mg (2.3 g) was added to 3.21 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 5.29 g of KOtBu in 25 mL of THF. Distillation gave 1.01 g (22.4%) of product determined to be >95% pure by GC: bp 105–110 °C at 5 Torr,  $^1\text{H}$  NMR  $\delta$  5.38 (m, 2H), 6.45 (dd, 1H), 7.28 (s, 4H);  $^{13}\text{C}$  NMR  $\delta$  116.2, 129.2, 131.2, 131.6, 132.4, 132.6; LRMS  $m/e$  170 ( $\text{M}^+$ ), 135 (base), 108, 91, 75; HRMS  $m/e$  calcd for  $\text{C}_8\text{H}_6\text{ClS}$  (M-H) 169.9957; found 169.9958;  $E_p^{\text{ox}}$  1.392 V.

**3-Chlorophenyl Vinyl Sulfide (3-Cl).** Using the above procedure, the Grignard reagent from 3-chloriodobenzene (14.507 g) and Mg (2.27 g) was added to 4.94 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 9.12 g of KOtBu in 25 mL of THF. Distillation gave 4.098 g (58.7%) of product determined to be >96% pure by GC: bp 105–110 °C at 5 Torr;  $^1\text{H}$  NMR  $\delta$  5.4 (m, 2H), 6.45 (dd, 1H), 7.18 (s, 3H), 7.33 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  117.5, 126.9, 127.8, 129.3, 130, 130.4, 135.5, 136.7; LRMS  $m/e$  170 ( $\text{M}^+$ ), 135 (base), 108, 91, 75; HRMS  $m/e$  calcd for  $\text{C}_8\text{H}_8\text{ClS}$  (M + H) 171.0035; found 171.0034;  $E_p^{\text{ox}}$  1.467 V.

**4-Trifluoromethylphenyl Vinyl Sulfide (4-CF<sub>3</sub>).** Using the above procedure, the Grignard reagent from 4-bromotrifluoromethylbenzene (11.123 g) and Mg (4.07 g) was added to 6.643 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 31 g of KOtBu in 100 mL of THF. Distillation gave 6.034 g (59.9%) of product determined to be >97% pure by GC: bp 80–83 °C at 5 Torr,  $^1\text{H}$  NMR  $\delta$  5.52 (m, 2H), 6.51 (dd, 1H), 7.38 (d, 2H), 7.55 (d, 2H);  $^{13}\text{C}$  NMR  $\delta$  119, 125.8, 125.9, 128.7, 129.5, 140.1; LRMS  $m/e$  204 ( $\text{M}^+$ ), 183, 159, 135 (base), 91, 69; HRMS  $m/e$  calcd for  $\text{C}_9\text{H}_7\text{F}_3\text{S}$  204.0221; found 204.0215  $E_p^{\text{ox}}$  1.604 V.

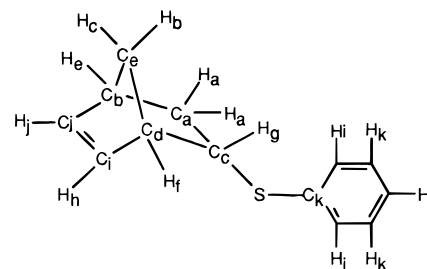
**3,5-Dichlorophenyl Vinyl Sulfide (3,5-DCI).** Using the above procedure, the Grignard reagent from 1-bromo-3,5-dichlorobenzene (22.62 g) and Mg (3.25 g) was added to 11.78 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 43.79 g of KOtBu in 100 mL of THF. Distillation gave 5.427 g (26.5%) of product determined to be >95% pure by GC: bp 110–115 °C at 3 Torr,  $^1\text{H}$  NMR  $\delta$  5.5 (m, 2H), 6.48 (dd, 1H), 7.18 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  119.6, 126.6, 126.9, 129.1, 135.3, 138.5; LRMS  $m/e$  204 ( $\text{M}^+$ ), 169, 134 (base); HRMS  $m/e$  calcd for  $\text{C}_8\text{H}_5\text{Cl}_2\text{S}$  (M-H) 203.9567 found 203.9565;  $E_p^{\text{ox}}$  1.612 V.

**4-(Methylthio)phenyl Vinyl Sulfide (4-MeS).** First, 9.62 g of thioanisole (77.4 mmol) in 60 mL of pentane was converted to 4-bromothioanisole by the slow addition of a solution of 12.4 g (mmol) of  $\text{Br}_2$  in 10 mL of pentane at room temperature. After 30 min, the solvent was removed, and the crude product was adsorbed onto 20 g of basic alumina and placed on top of 50 g of basic alumina. The product was flashed off the column using 9:1 hexane and EtOAc. After solvent removal, 14.3 g (87.4%) of 4-bromothioanisole was isolated. GC analysis of the crude product showed it was 93% pure, and it was used without further purification: LRMS 204 ( $\text{M}^+$ ), 202 ( $\text{M}^+$ , base), 158, 156, 108.

Then, using the above procedure, the Grignard reagent from 4-bromothioanisole (14.3 g) and Mg (4.24 g) was added to 8.13 g of 2-chloroethyl thiocyanate in 20 mL of THF. The elimination was carried out with 35 g of KOtBu in 100 mL of THF. Distillation gave 6.62 g (55.6%) of product determined to be >92.5% pure by GC: bp 100–110 °C at 1.5 Torr,  $^1\text{H}$  NMR  $\delta$  2.4 (s, 3H), 5.25 (m, 2H), 6.45 (dd, 1H), 7.11 (d, 2H), 7.25 (d, 2H);  $^{13}\text{C}$  NMR  $\delta$  15.8, 114.9, 127.2, 130.1, 131.7, 132.3, 138.3; LRMS  $m/e$  182 ( $\text{M}^+$ ), 167, 135 (base), 123, 108, 91; HRMS  $m/e$  calcd for  $\text{C}_9\text{H}_{11}\text{S}_2$  (M+H) 183.0302; found 183.0296;  $E_p^{\text{ox}}$  1.104 V.

**Synthesis of *endo*- and *exo*-5-(phenylthio)norbornene (3a,b).** A solution of phenyl vinyl sulfide (0.288 g, 2.1 mmol) and 1,3-cyclopentadiene (1.495 g 29.5 mmol) in 1.0 mL of  $\text{CH}_2\text{Cl}_2$  was added to 0.505 g (30%) of  $\mathbf{1}^+$  in 4 mL of  $\text{CH}_2\text{Cl}_2$  at 0 °C. After 10 min, 1 mL of saturated methanolic potassium carbonate was added, and the quenched reaction mixture was transferred to a separatory funnel containing  $\text{CH}_2\text{Cl}_2$  (50 mL) and washed with water (3  $\times$  50 mL). The organic phase was dried with  $\text{MgSO}_4$  and solvent removed at reduced pressure on a rotary evaporator. GC analysis of the crude product mixture showed an *endo/exo* ratio of 2.8:1. Column chromatography of the resulting residue was performed using neutral alumina (gradient

elution with hexane and  $\text{CH}_2\text{Cl}_2$ ), and it was found that the products were not separated from **1**. Next, column chromatography using silica gel (60 g, gradient elution with 500 mL of hexane INS followed by 250 mL of 9:1 hexane and ethyl acetate) was performed and gave 0.024 g (5.6%) of the *exo* isomer (90% pure by GC) and 0.103 g (24%) of the *endo* isomer (95% pure by GC). The isolated reaction products were characterized using TLC, GC, GC/MS, HRMS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and for the *endo* isomer 2D  $^1\text{H}$ – $^1\text{H}$  and  $^{13}\text{C}$ – $^1\text{H}$  NMR were collected to make a full spectral assignment:  $R_f(\text{exo}) = 0.5$  and  $R_f(\text{endo}) = 0.38$  on silica using pentane; *Exo*  $^1\text{H}$  NMR (250.1 Mhz)  $\delta$  1.5 (m, 2H), 1.75 (m, 2H), 2.85 (s, 1H), 2.93 (s, 1H), 3.08 (m, 1H), 6.06 (dd, 1H), 6.18 (dd, 1H), 7.15 (m, 1H), 7.2–7.4 (m, 4H);  $^{13}\text{C}$  NMR (62.9 MHz)  $\delta$  33.8, 41.7, 44.4, 45.9, 47.3, 125.6, 128.7, 129.1, 134.7, 137.8, 138.1; LRMS  $m/e$  202 ( $\text{M}^+$ ), 136 (base), 109, 91, 65. HRMS  $m/e$  calcd for  $\text{C}_{13}\text{H}_{14}\text{S}$  202.0816; found 202.08222; *Endo*  $^1\text{H}$  NMR (500.1 MHz)  $\delta$  0.9 (m, 1H<sub>a</sub>), 1.25 (d, 1H<sub>b</sub>), 1.48 (m, 1H<sub>c</sub>), 2.2 (m, 1H<sub>d</sub>), 2.85 (br s, 1 H<sub>e</sub>), 3.02 (br s, 1H<sub>f</sub>), 3.6 (m, 1H<sub>g</sub>), 6.05 (dd, 1H<sub>h</sub>), 6.2 (dd, 1H<sub>i</sub>), 7.08 (m, 1H<sub>j</sub>), 7.19 (m, 2H<sub>k</sub>), 7.28 (m, 2H<sub>l</sub>);  $^{13}\text{C}$  NMR (125.8 Mhz)  $\delta$  (a) 34.5, (b) 52.6, (c) 45.7, (d) 46.5, (e) 48.8, (f) 125.7, (g) 128.7, (h) 129.5, (i) 132.9, (j) 137.4, (k) 137.7; LRMS  $m/e$  202 ( $\text{M}^+$ ), 136 (base), 109, 91, 65; HRMS  $m/e$  calcd for  $\text{C}_{13}\text{H}_{14}\text{S}$  202.0816; found 202.08221.



3a (Y=H)

**General Procedure for the Synthesis of Substituted Phenylthio-norbornenes.** To 0.2 mmol of substituted aryl vinyl sulfide in 1 mL of  $\text{CH}_2\text{Cl}_2$  at 0 °C was added a 5-fold excess of 1,3-cyclopentadiene followed by 10% of  $\mathbf{1}^+$ . The reaction was stirred for 2 min and quenched with 0.5 mL of saturated methanolic potassium carbonate. The quenched reaction mixture was diluted with 5 mL of pentane and washed once with 5 mL of water, and the organic layer dried over  $\text{MgSO}_4$ , followed by solvent removal at reduced pressure on a rotary evaporator. The percent conversion was determined by GC, and the product identity was confirmed by GC/MS. The *endo/exo* ratio determined by GC was approximately 3:1 in all cases.

**5-(4-Methoxyphenylthio)norbornene.** Conversion 35.9%: LRMS  $m/e$  232 ( $\text{M}^+$ ), 166 (base).

**5-(4-Methylphenylthio)norbornene.** Conversion 38.4%: LRMS  $m/e$  216 ( $\text{M}^+$ ), 150 (base).

**5-(4-Phenylthio)norbornene.** Conversion 56.8%: LRMS  $m/e$  278 ( $\text{M}^+$ ), 212 (base).

**5-(3-Methylphenylthio)norbornene.** Conversion 28.8%: LRMS  $m/e$  216 ( $\text{M}^+$ ), 150, 135 (base).

**5-(4-Bromophenylthio)norbornene.** Conversion 6.9%: LRMS  $m/e$  282 ( $\text{M}^+$ ), 216, 135 (base).

**5-(3-Chlorophenylthio)norbornene.** Conversion 5.7%: LRMS  $m/e$  236 ( $\text{M}^+$ ), 170, 135 (base).

**5-(4-Trifluoromethylphenylthio)norbornene.** Conversion 2.0%: LRMS  $m/e$  270 ( $\text{M}^+$ ), 204, 135 (base).

**5-3,5-Dichlorophenylthio)norbornene.** Conversion 1.9%: LRMS  $m/e$  270, 204 (base), 169, 134.

**Reaction of Phenyl Vinyl Sulfide with 1,3-Cyclopentadiene under Photosensitized Electron Transfer Conditions.** To a dry Pyrex test tube was added 0.11 g (mol) of phenyl vinyl sulfide, 0.02 g (%) of 1,4-dicyanobenzene, 0.44 g (mol) of 1,3-cyclopentadiene, and 20 mL of  $\text{CH}_3\text{CN}$ . The test tube was placed inside a uranium filter in a 20 °C water bath and irradiated with a medium pressure mercury lamp. The progress of the reaction was monitored by GC. After 3 h, GC analysis showed 3% of the Diels–Alder cross adduct with an *endo/exo* ratio of 3:1. After 24 h, GC analysis showed 20% of the Diels–

Alder cross adduct with an *endo/exo* ratio of 2.9:1. The amount of conversion and the *endo/exo* ratio was found to be the same at 48 h.

**Reaction of Phenyl Vinyl Sulfide with 1,3-Cyclopentadiene using Triflic Acid in Dichloromethane.** To 0.064 g (mol) of phenyl vinyl sulfide and 0.219 g (mol) of 1,3-cyclopentadiene at 0 °C was added 3 drops (20–30%) of triflic acid. After 5 min, the reaction was quenched with 5 mL of saturated K<sub>2</sub>CO<sub>3</sub> in MeOH. GC analysis showed two peaks (1:7 ratio) at retention times slightly longer than those of the Diels–Alder cross adducts. GC/MS analysis showed that both acid cross adducts had the same molecular weight and that, unlike the Diels–Alder cross adducts, the molecular ion was the base peak in the mass spectrum: LRMS 202 (M<sup>+</sup>, base), 187, 179, 161, 147, 134, 115, 91, 77.

**Reaction of Phenyl Vinyl Sulfide with 1,3-Cyclopentadiene using 1<sup>+</sup> in the Presence of 2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP) in Dichloromethane.** To 0.051 g (0.375 mmol) of phenyl vinyl sulfide, 0.168 g (mol) of 1,3-cyclopentadiene, and 0.053 g (0.259 mmol) of DTBMP in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C was added 0.122 g (40%) of 1<sup>+</sup>. After 15 min the reaction was quenched with 5 mL of saturated K<sub>2</sub>CO<sub>3</sub> in MeOH. GC analysis indicated that the reaction had gone to 15% conversion, and the *endo/exo* ratio was 2.8:1. There were no peaks observed for the acid cross adducts.

**Synthesis of *cis*-Phenyl Vinyl Sulfide- $\beta$ -d<sub>1</sub>.** First, 12.9 g (0.133 mol) of *cis*-1,2-dichloroethene was converted to *cis*-1,2-bis(phenylthio)ethene (BPTE) by treatment with 25.8 g (0.234 mol) of thiophenol and 20 g (0.357 mol) of KOH in 350 mL of refluxing EtOH for 4 h.<sup>27</sup> Recrystallization from hexane gave 19.7 g (57.4%) BPTE which was found to be 99% pure by GC: mp 31–32.5 °C; <sup>1</sup>H NMR  $\delta$  6.5 (s, 2H), 7.1–7.5 (m, 10H); <sup>13</sup>C NMR  $\delta$  124.8, 126.8, 129.0, 129.3, 123.1; E<sub>p</sub><sup>ox</sup> 1.1 38 V.

Next, 8.72 (35.5 mmol) of BPTE in 10 mL of dry Et<sub>2</sub>O was converted to phenylthioacetylene (PTA) by slow addition (~2 min) to 70 mmol of *n*-butyllithium (7 mL of 10 M solution in hexanes) in 20 mL of dry Et<sub>2</sub>O at –10 °C.<sup>26</sup> Distillation gave 4.0 g of PTA: bp 78–80 °C at 4 Torr; <sup>1</sup>H NMR  $\delta$  3.25 (s, 1H), 7.2–7.5 (m, 5H); <sup>13</sup>C NMR  $\delta$  71, 86.9, 126.5, 126.7, 129.2, 131.4; LRMS *m/e* 134 (M<sup>+</sup>, base), 109, 92, 91, 77.

Finally, the above PTA was dissolved in 5 mL of dry Et<sub>2</sub>O and added dropwise to 20 mL of a 1 M solution of LAD at –10 °C. Following the addition, the reaction was allowed to warm to room temperature and worked up. Distillation of the crude product afforded 2 mL of *cis*-phenyl vinyl sulfide- $\beta$ -d<sub>1</sub>:<sup>21</sup> bp 55–56 °C at 2 Torr; <sup>1</sup>H NMR  $\delta$  5.3 (d, 1H), 6.5 (dt, 1H), 7.2–7.4 (m, 5H); LRMS *m/e* 137 (M<sup>+</sup>), 109 (base), 91.

**Test for Stereospecificity in the Reaction of Phenyl Vinyl Sulfide with 1,3-Cyclopentadiene Catalyzed by 1<sup>+</sup>.** *cis*-Phenyl vinyl sulfide- $\beta$ -d<sub>1</sub> was reacted with 1,3-cyclopentadiene, and the starting material and products isolated using the procedure reported for the synthesis and isolation of *exo* and *endo* 5-phenylthionorbomene. The recovered starting material was found to be ~45% isomerized by <sup>1</sup>H NMR. The *endo* isomer (90% pure by GC) was found to be 25% isomerized: <sup>1</sup>H NMR  $\delta$  0.9 (br d, 0.25H), 1.3 (d, 1H), 1.55 (m, 1H), 2.4 (br d, 0.75H), 2.9 (br s, 1H), 3.1 (br s, 1H), 3.7 (dd, 1H), 6.1 (m, 1H), 6.3 (m, 1H), 7.1–4 (m, 5H); <sup>13</sup>C NMR  $\delta$  34 (t), 42.5, 45.6, 4.4, 48.8, 125.7, 128.7, 129.5, 133, 137.4; LRMS *m/e* 203 (M<sup>+</sup>), 137 (base), 109, 92; HRMS *m/e* calcd for C<sub>13</sub>H<sub>14</sub><sup>2</sup>HS (M + H) 204.0957; found 204.0959.

**Stability of the Deuterated *Endo* Cross Adduct in the presence of 1<sup>+</sup> in Dichloromethane.** The above deuterated *endo* cross adduct (0.025 g) was dissolved in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C, and 0.012 g (12%) of 1<sup>+</sup> was added. After 2 min, the reaction was quenched and analyzed by GC. It was found that no isomerization had taken place.

**General Procedure for the Competitive Cycloadditions of Substituted Aryl Vinyl Sulfides with 1,3-Cyclopentadiene Catalyzed by 1<sup>+</sup> in Dichloromethane.** A stock solution was prepared in a dry 10 mL volumetric flask by adding a known amount of naphthalene, equimolar amounts (0.6–1.0 mmol) of two aryl vinyl sulfides that were of similar reactivity, and a 5-fold excess (based on the sum of the molar amounts of the aryl vinyl sulfides) of 1,3-cyclopentadiene. Then CH<sub>2</sub>Cl<sub>2</sub>, precooled to 0 °C, was added to the mark. A similar stock solution of 1<sup>+</sup> was prepared, and trial runs were performed by adding small amounts (0.2–1.0 mL, 0.1–10% 1<sup>+</sup>) of this stock solution to 1 mL aliquots of the aryl vinyl sulfide solution until conditions that gave

<10% conversion in 1 min were found. The reactions were quenched with 0.3 mL of saturated methanolic potassium carbonate. Then 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added, followed by washing twice with 5 mL portions of water and drying over MgSO<sub>4</sub>. In all cases the results were the average of four runs analyzed twice each. The calculated mass balances for all relative rate analyses were commonly over 95% but in a few instances were as low as 85%. Response factors for all relative rate analyses were determined by dilution of a portion of the unused aryl vinyl sulfide stock solution: log *k*<sub>rel</sub> 4-MeO 1.03, 4-Me 0.922, 3-Me 0.45, 4-Br 0.79, 3-Cl 1.48, 4-CF<sub>3</sub> 2.02.

**Effect of the Concentration of 1,3-Cyclopentadiene upon the Relative Rate Ratio of 4-Methoxyphenyl Vinyl Sulfide vs Methylphenyl Vinyl Sulfide.** A stock solution was prepared in a dry 10 mL volumetric flask by adding a known amount of naphthalene followed by equimolar amounts of 4-methoxyphenyl vinyl sulfide and 4-methylphenyl vinyl sulfide. The flask was then filled to the mark with precooled CH<sub>2</sub>Cl<sub>2</sub>. Four stock solutions of 1,3-cyclopentadiene were prepared in a similar manner with the following excesses based on the sum of the molar amounts of the two sulfides: 5, 2.4, 0.54, and 0.2. Aliquots (1 mL) of each stock solution were added to a vial followed by a solution of 1<sup>+</sup> to give a conversion of less than 10% in the more reactive compound. Each relative excess was measured in duplicate. *k*(4-MeO)/*k*(4-CH<sub>3</sub>) for 5 $\times$  = 2.76, 2.4 $\times$  = 2.74, 0.54 $\times$  = 2.67, 0.2 $\times$  = 2.78; average = 2.73.

**General Procedure for the Competitive Cycloadditions of Substituted Aryl Vinyl Sulfides with 1,3-Cyclopentadiene under Electrochemical Conditions.** A stock solution was prepared in a dry 10 mL volumetric flask by adding a known amount of naphthalene, equimolar amounts (0.6–1.0 mmol) of two aryl vinyl sulfides that were of similar reactivity, and a 5-fold excess (based on the sum of the molar amounts of the aryl vinyl sulfides) of 1,3-cyclopentadiene. Then a 0.1 M solution of lithium perchlorate in acetonitrile was added to the mark. A 1 mL aliquot of the stock solution was added to 9 mL of electrolyte solution (0.1 M lithium perchlorate in acetonitrile). The reaction was run at a constant potential of 0.8 V (*vs* Ag/Ag<sup>+</sup>) using a divided cell equipped with a reticulated vitreous carbon working electrode (anode), a reticulated vitreous carbon counter electrode, and a Ag/Ag<sup>+</sup> reference electrode (calibrated against ferrocene/ferrocene<sup>+</sup>). After passing 1 C of current, the reaction mixture was transferred to a test tube followed by the addition of 5 mL of H<sub>2</sub>O and 3 mL of hexane. The test tube was vigorously shaken, and the layers allowed to separate. GC analysis was carried out on the hexane layer, and the standard was treated in a similar way. In all cases the results were the average of three runs analyzed twice each, and the recovery was >95%. The average *endo/exo* ratio was 2.2:1: log *k*<sub>rel</sub> 4-Me 0.614, 3-Me 0.12, 4-Br 0.501, 3-Cl 1.27.

**General Procedure for the Competitive Cycloadditions of Substituted Aryl Vinyl Sulfides with 1,3-Cyclopentadiene Catalyzed by 1<sup>+</sup> in Acetonitrile.** A stock solution was prepared in a dry 10 mL volumetric flask by adding a known amount of naphthalene, equimolar amounts (0.6–1.0 mmol) of two aryl vinyl sulfides that were of similar reactivity, and a 5-fold excess (based on the sum of the molar amounts of the aryl vinyl sulfides) of 1,3-cyclopentadiene. Then acetonitrile, precooled to 0 °C, was added to the mark. A similar stock solution of 1<sup>+</sup> was prepared, and trial runs were performed by adding small amounts (0.2–1.0 mL, 0.1–10% 1<sup>+</sup>) of this stock solution to 1 mL aliquots of the aryl vinyl sulfide stock solution until conditions that gave <10% conversion in 1 min were found. The reactions were quenched with 0.3 mL of saturated methanolic potassium carbonate. Then 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added, followed by washing twice with 5 mL portions of water and drying over MgSO<sub>4</sub>. In all cases the results were the average of three runs analyzed twice each, and the recovery was >95%. The average *endo/exo* ratio was 2.7:1: log *k*<sub>rel</sub> 4-MeO 1.21, 4-Me 0.815, 3-Me 0.327, 4-Br 0.652, 3-Cl 1.34, 3,5-DCI 1.95.

**General Procedure for the Competitive Cycloadditions of Substituted Aryl Vinyl Sulfides with 1,3-Cyclopentadiene Catalyzed by 1<sup>+</sup> in Acetonitrile Containing 0.1 M Lithium Perchlorate.** Equimolar amounts of two aryl vinyl sulfides were weighed into a dry vial along with 0.25 g of 1,3-cyclopentadiene and 5 mL of a 0.1 M solution of lithium perchlorate in acetonitrile. The competitive experiments were conducted in a manner similar to the previous aryl vinyl sulfide experiments except that the results are not calibrated, and



two runs analyzed twice each were averaged to obtain each data point. The average *endo/exo* ratio was 2.5:1:  $\log k_{\text{rel}}$  4-MeO 0.96, 4-Me 0.64, 3-Me 0.26, 4-Br 0.64, 3-Cl 1.3.

**Effect of Added Triarylamine on the Absolute Reaction Rates of Cycloaddition and the Selectivity of the Cycloaddition of Substituted Aryl Vinyl Sulfides with 1,3-Cyclopentadiene Catalyzed by  $1^{++}$  in Dichloromethane.** A stock solution was prepared in a dry 10 mL volumetric flask by adding a known amount of naphthalene, equimolar amounts (0.6–1.0 mmol) of two aryl vinyl sulfides that were of similar reactivity, and a 5-fold excess (based on the sum of the molar amounts of the aryl vinyl sulfides) of 1,3-cyclopentadiene. Then  $\text{CH}_2\text{Cl}_2$ , precooled to 0 °C, was added to the mark. A similar stock solution of  $1^{++}$  was prepared. Aliquots (1 mL) of the stock solution were added to a series of vials containing 1 (0, 25, 50, 100, and 200 mol %) followed by the addition of equal volumes of the  $1^{++}$  solution. After

2 min, the reactions were quenched with 0.3 mL of saturated methanolic potassium carbonate. Then 2 mL of  $\text{CH}_2\text{Cl}_2$  was added, followed by washing twice with 5 mL portions of water and drying over  $\text{MgSO}_4$ . No change in the rates or selectivity was observed.

**Effect of the Concentration of 1,3-Cyclopentadiene upon the Absolute Reaction Rates of Cycloaddition.** Single point measurements were obtained for identical reactions run for 1 min at two concentrations of 1,3-cyclopentadiene using three different amounts of  $1^{++}$ . Doubling the concentration of the diene gave the following results: 4-Me 0.89, H 1.05, 3-Cl 0.80.

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