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Convenient criterion for the distinction between electrophilic and electron transfer reactions of electron-rich alkenes

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ABSTRACT: Both experimental and theoretical studies confirm that the formation of aryl vinyl ether and aryl vinyl sulfide cation radicals from the corresponding neutral substrates correlates with the Brown σ^+ parameters as opposed to Hammett σ values. Peak oxidation potentials for both classes of substrates correlate preferentially with σ^+, as do gas-phase ionization energies calculated by both semi-empirical and *ab initio* methods. In contrast, the protonation energies of the same substrates, which relate to carbocation formation, correlate preferentially with σ values, as do rates of protonation and other electrophilic additions. These observations permit a sharp distinction between electrophilic and electron transfer reactions of these two common classes of electron-rich substrates. Using this criterion, the cycloadditions of tetracyanoethylene to these substrates are found to proceed via an electrophilic mechanism, rather than by a previously proposed electron transfer mechanism. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: electrophilic reactions; electron transfer reactions; electron-rich alkenes; tetracyanoethylene

INTRODUCTION

More than three decades after the recognition of the electron transfer (ET) mechanism as an alternative to the familiar polar mechanism for covalent bond formation, the distinction between polar and ET mechanisms continues to be problematic. The seminal proposal by Kosower[1] of an ET mechanism for the cycloaddition of tetracyanoethylene (TCNE) to electron-rich alkenes is illustrative (Scheme 1). The difficulty in characterizing such an ET mechanism is inherent in the potentially very short lifetimes of caged ion radical pair intermediates. In principle, ultrafast intramolecular cation radical (or anion radical) probes are capable of detecting even the shortest-lived intermediates, but the cation radical probes developed thus far are not capable of detecting intermediates having lifetimes of 10^{-12} s or less.[2] In the present work, a surprisingly straightforward and convenient criterion for the differentiation of electrophilic and ET reactions of certain electron rich alkenes was developed.

RESULTS AND DISCUSSION

Electrophilic addition to an aryl vinyl ether (or sulfide or selenide) yields a cationic intermediate (e.g **1,** Scheme 2) in which the carbocation center is homobenzylic (see canonical structures **1** and **2a**). In the terminology of resonance theory, the positive charge is also delocalized on to the benzylic heteroatom (canonical structure **2b**), but is not significantly delocalized on to the ring π-electron system or on to a *para* resonance electron-donating substituent, since this would require expansion of the heteroatom octet (structure **2c**). Since the quinonoidal type resonance structure (**2c**) required by the classical σ/σ^+ paradigm[3] for a correlation of substituent effects with the Hammett–Brown σ^+ parameter is invalid, it is predicted that substituent effects in electrophilic additions to these substrates should correlate with the Hammett σ parameter. The application of the conventional paradigm to an ET reaction which forms a substrate cation radical is less straightforward, but this process appeared highly likely to correlate with σ^+. In part, our reasoning was that the cation radical moiety (or hole) must be delocalized substantially over both the aromatic ring and the ethenic double bond, and positive charge situated directly on the ring is known to be stabilized by the enhanced resonance effect of *para* π-donor substitutents which differentiates σ^+ from σ.[3] If this intuitive analysis can be substantiated, the σ/σ^+ criterion would provide an unusually straightforward and convenient method for distinguishing electrophilic and ET mechanisms for a range of functionality which should be especially amenable to an ionization mechanism. The validity of the foregoing analysis is strongly supported by both theoretical and experimental studies to be detailed herein, and the results provide an unequivocal assignment

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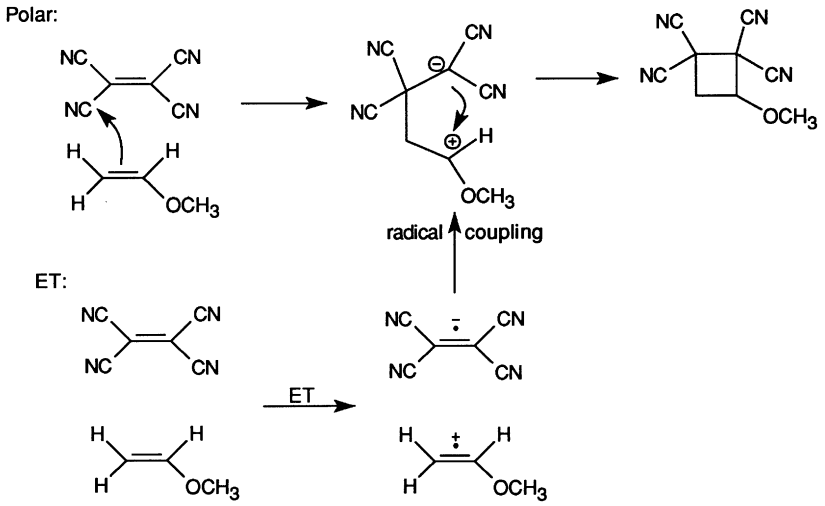
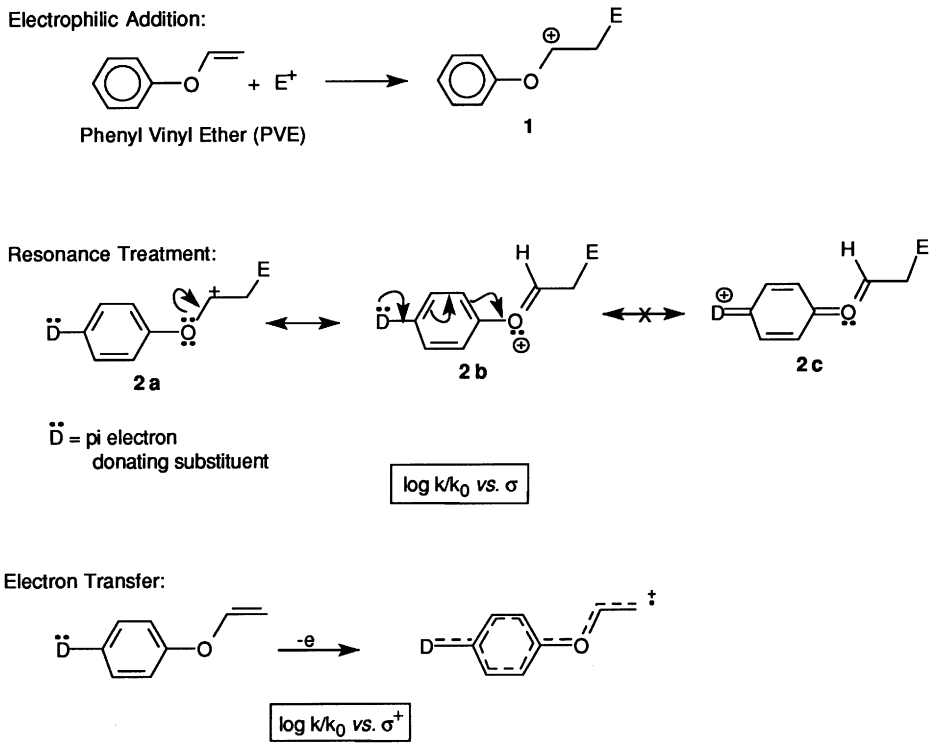


Scheme 1. Polar and ET mechanisms for the cycloaddition of TCNE with methyl vinyl ether

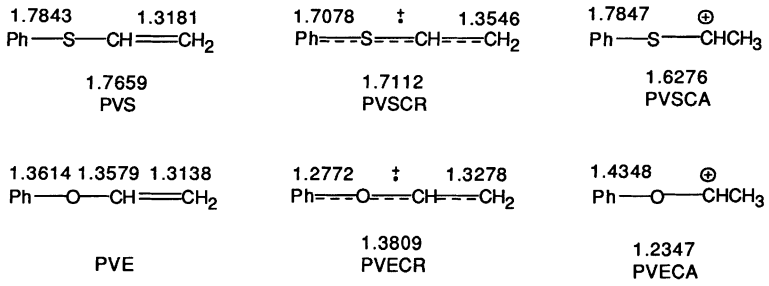
for the mechanism of the TCNE/electron-rich alkene cycloadditions.

Theoretical studies

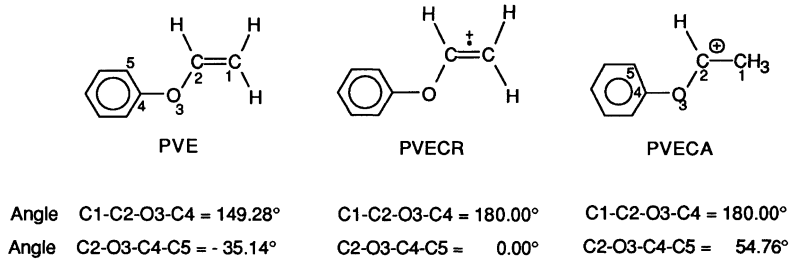
Geometric considerations. *Ab initio* SCF MO calculations were carried out at the 6–31G*//6–31G* level (i.e. fully geometry optimized using the 6–31G* basis set) for phenyl vinyl ether (PVE), phenyl vinyl sulfide (PVS) and the corresponding cation radicals (PVECR, PVSCR) and conjugate acids [the 1-phenoxyethyl carbocation (PVECA) and the 1-phenylthioethyl carbocation (PVSCA)]. *Ab initio* calculations were carried out using the Gaussian 94 program on the Cray YMP computer at the University of Texas High Performance Computation Facility. The optimizations were carried out using the indicated basis set without imposing any synmmetry restraints. All doublet species were calculated using the UHF procedure; otherwise the RHF procedure was used. The optimized geometries are available as supplementary material. Selected bond lengths in these six species are



Scheme 2. The σ (electrophilic)/σ^+ (ET) criterion



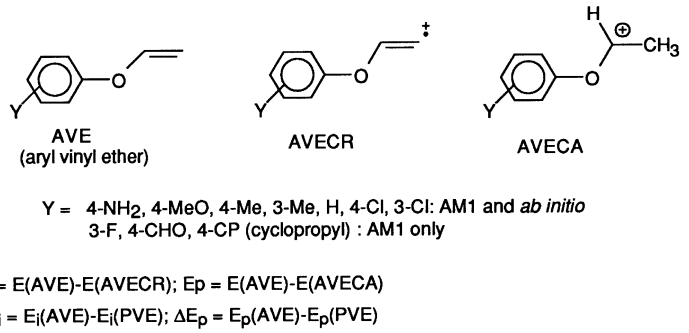
Scheme 3. Selected bond lengths (Å) of phenyl vinyl ether, phenyl vinyl sulfide and the corresponding cation radicals and conjugate acids optimized at the 6–31G*//6–31G* level



Scheme 4. Conformation of the side-chain in phenyl vinyl ether (PVE) and its cation radical (PVECR) and conjugate acid (PVECA): 6–31G*//6–31G*

particularly pertinent (Scheme 3). Especially noteworthy is the observation that the phenyl–sulfur bond of PVSCA (1.7847Å) is virtually identical with that in PVS (1.7843Å), suggesting that there is no significant contribution from a canonical structure such as **2c,** which should shorten the phenyl–sulfur bond. As would be expected from structure **2b,** the bond from sulfur to the carbocation center is much shorter in PVSCA (1.6276Å) than in PVS (1.7659Å). In sharp contrast, the phenyl-sulfur bond in PVSCR (1.7078Å) is much shorter than that in PVE (1.7843Å) and is even just slightly shorter than the vinyl-sulfur bond (1.7112Å). The implication is that the sulfur in PVSCR is more strongly conjugated with the phenyl ring in PVSCR than in PVS and that conjugation with the phenyl and vinyl group is about equally strong. Analogous relationships exist in the case of PVE, PVECR and PVECA. Interestingly, the phenyl–oxygen bond in PVECA is actually longer (1.4348Å) than in PVE (1.3614Å), indicating that strong conjugation of the oxygen atom with the carbocation center weakens the conjugative interaction of the oxygen atom (as an electron donor) with the phenyl ring. The phenyl–oxygen bond in PVECR, on the other hand, is much shorter (1.2772Å) than that in PVE.

The conformations of the side-chains in the PVE, PVECR and PVECA lend additional credence to the proposal that the oxygen atom of PVECA is unable to act as a π-electron acceptor in relation to the phenyl ring (Scheme 4). Whereas the side-chain in PVECR is rigorously planar with the phenyl ring, that in PVECA is twisted by 54.7° out of the ring plane. Even in PVE, the twist angle is only 35°. The highly twisted structure of PVECA would not appear reasonable if canonical structure **2c** were contributing very significantly.



Scheme 5. Theoretical ionization energies and protonation energies

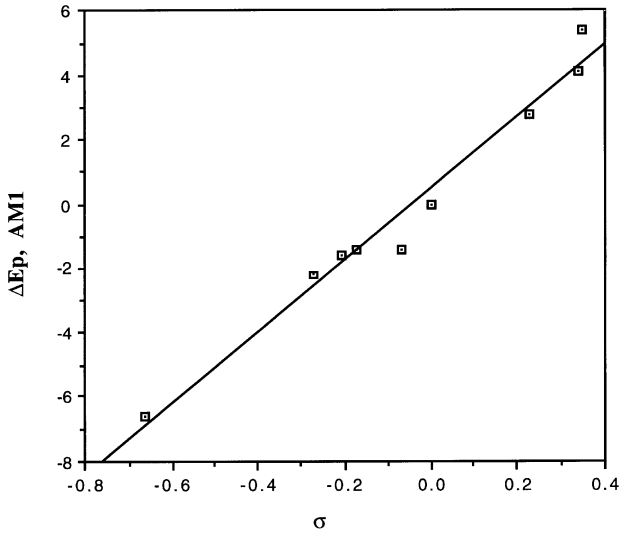


Figure 1. Plot of relative AM1 protonation energies (ΔE_p) of aryl vinyl ethers *vs* Hammett σ. The correlation equation is $\Delta E_p = 11.115\sigma + 0.46577$ ($r^2 = 0.974$)

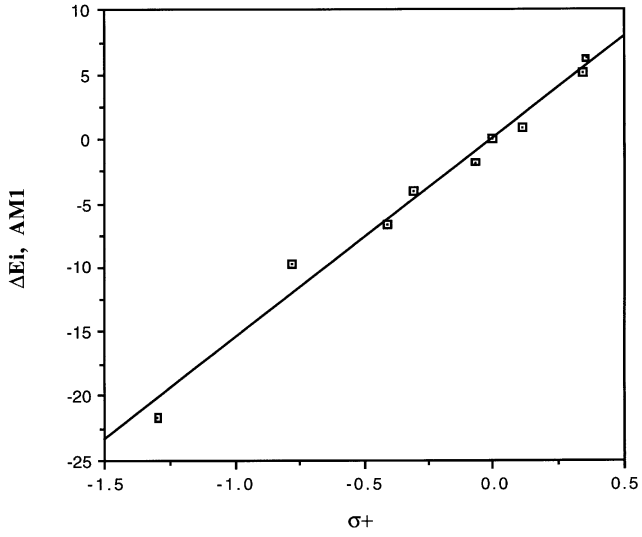


Figure 3. Plot of relative AM1 ionization energies (ΔE_i) of aryl vinyl ethers *vs* σ^+. The correlation equation is $\Delta E_i = 15.640\ \sigma^+ + 0.069488$ ($r^2 = 0.982$)

Frontier orbital considerations. The leading interaction in the stabilization of a carbocation center by a resonance (π) electron-donating *para* substituent is expected to be that involving the substituent HOMO and the carbocation LUMO. The density distribution of the LUMO of PVECA is therefore of particular interest and is depicted in Plate 1. Graphic illustrations of the LUMO and SOMO were generated using the program MACSPARTAN. Blue regions correspond to the highest density and red to the lowest density. It is evident from Plate 1 that this LUMO is highly localized upon the side-chain and that very little density is delocalized on to the *para* position. In contrast, the SOMO of PVECR, which should reflect the charge distribution in the frontier orbital approximation, reveals an especially high density at the *para* position (Figure 1). Consequently, the frontier orbital interaction is considered likely to be extremely weak in PVECA. This interaction should correspond roughly to canonical structure **2c.**

Linear free energy correlations. The most direct theoretical test of the proposed σ/σ^+ criterion would appear to be the calculation of ionization energies (E_i) and protonation energies (E_p) of a series of *meta*- and *para*-substituted phenyl vinyl ethers (Scheme 5). Such calculations have been carried out in this study at both the semi-empirical (AM1) and *ab initio* (MP2/6–31G*//6–31G) levels of theory. The gas-phase ionization energy,

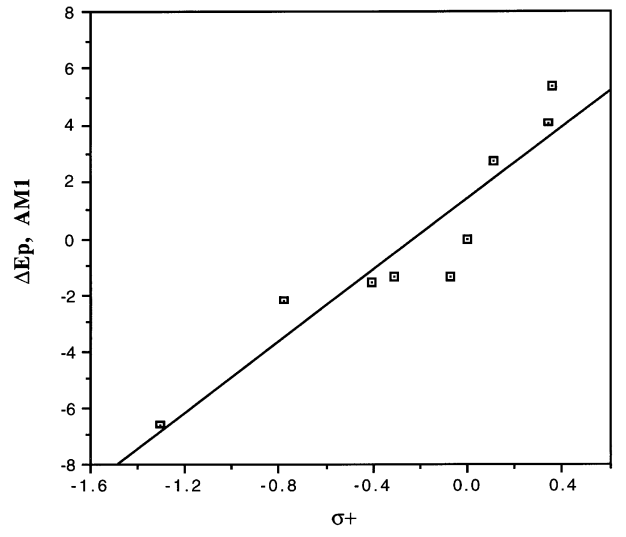


Figure 2. Plot of relative AM1 protonation energies (ΔE_p) of aryl vinyl ethers *vs* Brown σ^+. The correlation equation is $\Delta E_p = 6.3438\ \sigma^+ + 1.3567$ ($r^2 = 0.870$)

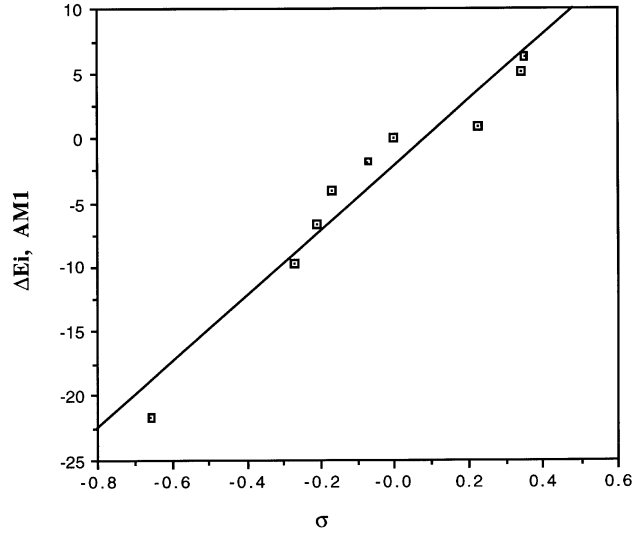


Figure 4. Plot of relative AM1 ionization energies (ΔE_i) of aryl vinyl ethers *vs* σ. The correlation equation is $\Delta E_i = 25.384\ \sigma - 2.2303$ ($r^2 = 0.943$)

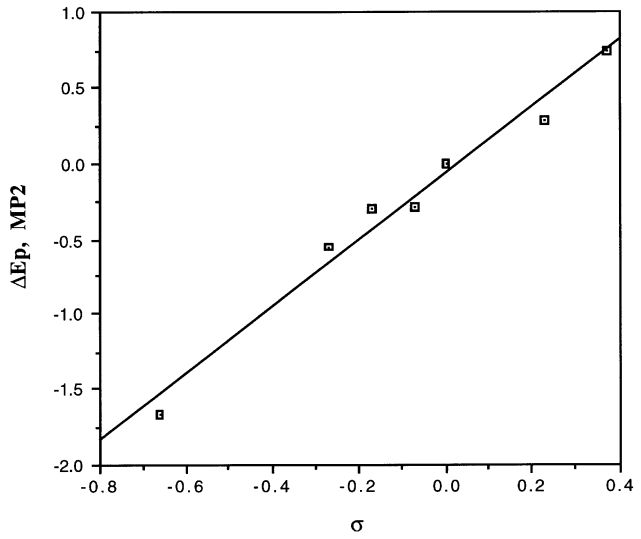


Figure 5. Plot of relative *ab initio* MP2/6–31G*//6–31G protonation energies (ΔE_p) ($\times 100$ in au) of aryl vinyl ethers *vs* σ. The correlation equation is $\Delta E_p = 0.22317\ \sigma - 0.000704$ ($r^2 = 0.977$)

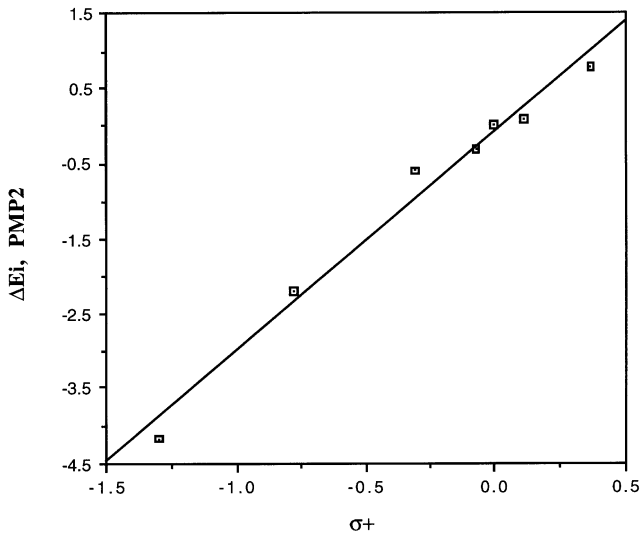


Figure 7. Plot of relative *ab initio* PMP2/6–31G*//6–31G ionization energies (ΔE_i) ($\times 100$) of aryl vinyl ethers *vs* σ^+. The correlation equation is $\Delta E_i = 0.029245\ \sigma^+ - 0.00087$ ($r^2 = 0.980$)

E_i, is defined here as the energy difference between the neutral molecule and the corresponding cation radical, both fully geometry optimized without symmetry constraints. Calculations for the cation radicals are of the unrestricted Hartree–Fock (UHF) type. The gas-phase protonation energy (proton affinity, E_p) is defined as the energy difference between the neutral molecule and the corresponding conjugate acid (carbocation). The terms ΔE_i and ΔE_p refer to the differences in E_i and E_p, respectively, of a substituted PVE and unsubstituted PVE (Scheme 5). The correlation of the AM1 ΔE_p with σ (Figure 1) can be seen to be fairly good ($r^2 = 0.974$), whereas the correlation of ΔE_p with σ^+ is poor (Figure 2; $r^2 = 0.870$, substituent parameters were taken from Ref. 4.) In contrast, the correlation of ΔE_i with σ^+ is satisfactory (Figure 3; $r^2 = 0.982$), while the correlation of ΔE_i with σ is much less so (Figure 4; $r^2 = 0.943$). The slope of the plot of ΔE_i *vs* σ^+ translates into a Hammett ρ value of -11.5, whereas the slope of the plot of ΔE_p *vs* σ is equivalent to $\rho = -8.2$ (both in the gas phase).

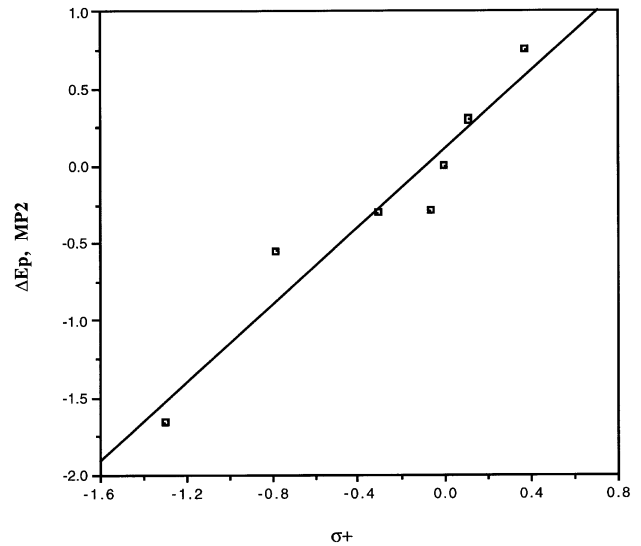


Figure 6. Plot of relative *ab initio* MP2/6–31G*//6–31G protonation energies (ΔE_p) ($\times 100$) of aryl vinyl ethers *vs* σ^+. The correlation equation is $\Delta E_p = 0.012644\ \sigma + 0.0011$ ($r^2 = 0.924$)

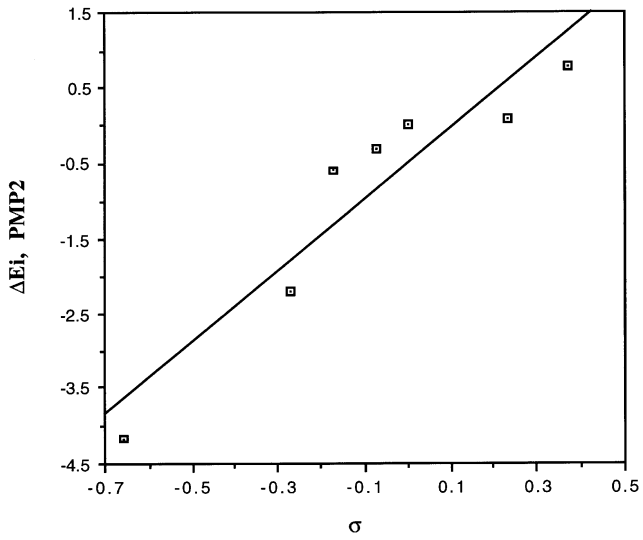


Figure 8. Plot of relative *ab initio* PMP2/6–31G*//6–31G ionization energies (ΔE_i) ($\times 100$) of aryl vinyl sulfides *vs* σ. The correlation equation is $\Delta E_i = 0.047355\ \sigma - 0.00529$ ($r^2 = 0.886$)

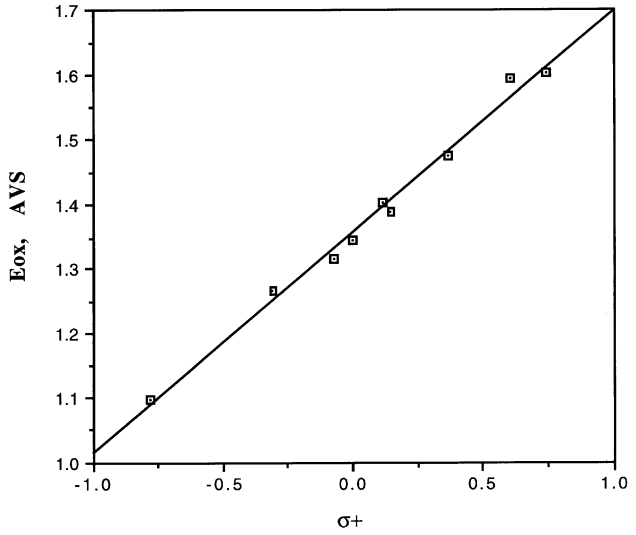


Figure 9. Plot of peak oxidation potentials (E_{OX}, V *vs* SCE) of aryl vinyl sulfides by DPV in acetonitrile *vs* σ^+. The correlation equation is $\Delta E_{OX} = 0.34113\sigma^+ + 1.3563$ ($r^2 = 0.990$)

The corresponding *ab initio* results further support the validity of the proposed σ/σ^+ criterion. The results refer to MP2/6–31G* point calculations at the fully optimized 6–31G geometries of each species. The ΔE_p *vs* σ correlation (Figure 5) is clearly superior ($r^2 = 0.977$) to that for ΔE_p *vs* σ^+ (Figure 6, $r^2 = 0.924$). The ionization energies, on the other hand, correlate nicely with σ^+ (Figure 7, $r^2 = 0.981$) and poorly with σ (Figure 8, $r^2 = 0.886$). The slopes of the plots of ΔE_i and ΔE_p *vs* σ^+ and σ, respectively, correspond to values of $\rho = -13.5$ and -10.2 for the ionization and protonation, respectively, of phenyl vinyl ethers in the gas phase. The slope of the ΔE_i and ΔE_p *vs* σ or σ^+ plots is related to the reaction constant by the following equation, where the ΔEs are expressed in kcal mol^{-1}.

$$\rho = (\text{slope})(1000)/(-2.303)(1.987)(298)$$

For *ab initio* energies expressed in atomic units, the appropriate equation is

$$\rho = (\text{slope})(627.7)(1000)/(-2.303)(1.987)(298)$$

Finally, where energies are expressed in volts (E_{OX}), the appropriate equation is

$$\rho = (\text{slope})(23.06)(1000)/(-2.303)(1.987)(298)$$

Experimental tests

The proposed correlation of the ionization energies of AVE and AVS with σ^+ rather than with σ has been further examined by synthesizing and measuring the peak potentials for the ionization of a series of *meta*- and *para*-substituted phenyl vinyl sulfides (Table 1) and phenyl *cis*-propenyl ethers (Table 2). The correlations of these peak potentials (E_{OX}) with σ^+ and σ are depicted in Figures 9–12. The statistical treatments strongly support the correlation with σ^+, and *F*-tests[5] indicate that the distinction is valid in both reaction series at or above the 95% confidence level. The ρ values for the ionization of aryl propenyl ethers and aryl vinyl sulfides in acetonitrile solution at ambient temperatures are -7.6 and -5.8, respectively.

Table 1. Peak oxidation potentials (E_{OX}) for aryl vinyl sulfides in acetonitrile determined by differential pulse voltammetry

Substituent	E_{OX} (V *vs* SCE)	Substituent	E_{OX} (V *vs* SCE)
4-MeO	1.097	4-Br	1.389
4-Me	1.267	3-Cl	1.475
3-Me	1.314	4-CF_3	1.594
H	1.346	3,5-Cl_2	1.603
4-Cl	1.401		

Electrophilic additions to substituted PVEs[6], PVSs[7,8] and PVSes[9] have already been extensively investigated and found to correlate preferentially with Hammett σ values. These studies include kinetically controlled protonation of PVEs, PVSs and PVSes and trifluoroacetylation of PVSs, all involving reaction of an electrophile at the terminal carbon of the vinyl group.

CONCLUSIONS

An extensive array of theoretical and experimental evidence supports the contention that rates and equilibria in electrophilic additions to aryl vinyl ethers, sulfides and selenides preferentially correlate with Hammett σ values as opposed to Brown σ^+ values, but electron transfer (ionization) reactions of these same electron-rich alkenes correlate with the σ^+ parameter preferentially. Since these functional groups are among those which, because of the facility of their ionization, should be especially amenable to ET reactions, the σ/σ^+ criterion provides a particularly useful and convenient diagnostic test for electrophilic *vs* ET reaction modes. Finally, since the reactions of TCNE with aryl vinyl ethers, sulfides and selenides have all been found to correlate preferentially with σ,[10] these cycloadditions can be confidently assigned an electrophilic (polar) mechanism, and the hypothetical ET mechanism can be ruled out.

Table 2. Peak oxidation potentials (E_{OX}) for aryl *cis*-propenyl ethers determined by differential pulse voltammetry

Substituent	E_{OX} (V *vs* Ag/Ag$^+$)	Substituent	E_{OX} (V *vs* Ag/Ag$^+$)
4-MeO	1.197	3-Me	1.574
3,4-Me_2	1.408	H	1.601
4-Me	1.464	4-Br	1.621
3,5-Me_2	1.508	3-Cl	1.715

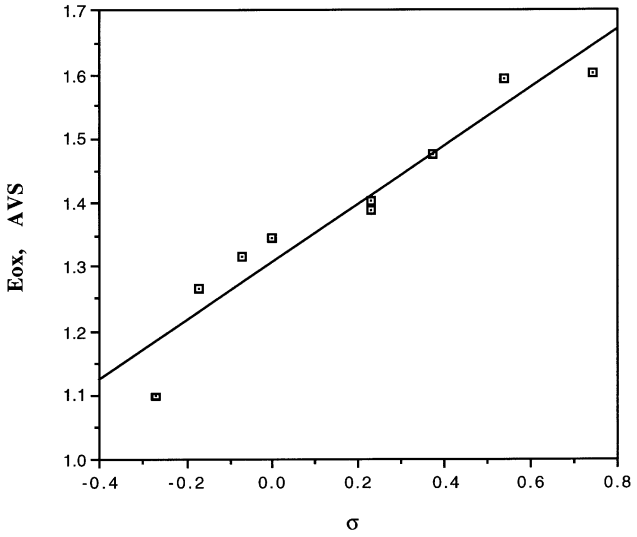


Figure 10. Plot of peak oxidation potentials (E_{OX}, V *vs* SCE) of aryl vinyl sulfides by DPV in acetonitrile *vs* σ. The correlation equation is $\Delta E_{OX} = 0.45472\ \sigma + 1.3065$ ($r^2 = 0.921$)

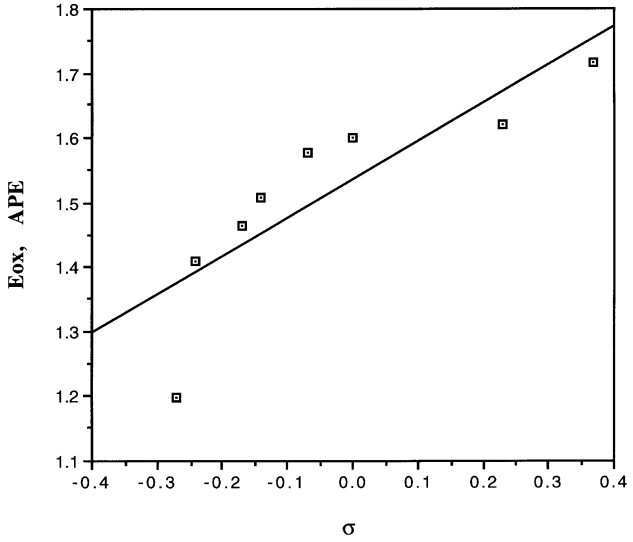


Figure 12. Plot of peak oxidation potentials (E_{OX}, V *vs* SCE) of aryl *cis*-propenyl ethers by DPV in acetonitrile *vs* σ. The correlation equation is $\Delta E_{OX} = 0.5900\ \sigma + 1.2324$ ($r^2 = 0.713$)

EXPERIMENTAL

Electrochemical measurements were carried out using a BAS 100 electrochemical analyzer in the differential pulse voltammetric (DPV) mode scanning in the range 500–1900 mV at a scan rate of 5 $mV^{-1}s$ with a pulse amplitude of 50 mV, a pulse width of 50 ms, a pulse period of 1000 ms and a sensitivity of 1×10^{-6}. The electrochemical cell was a divided cell equipped with a platinum disk working electrode (anode), a reticulated vitreous carbon counter electrode (cathode), attached to a copper wire and separated from the working electrode by a glass frit. An Ag/Ag^+ reference electrode (silver wire immersed in a solution of dried acetonitrile, 0.1 M in $AgNO_3$ and $LiClO_4$), calibrated *vs* the ferrocene/ferricinium ion couple, was placed in the anode compartment and separated from the bulk solution by a Vycor frit. The bulk solution consisted of the analyte (1–5 mg ml^{-1}) dissolved in anhydrous acetonitrile containing 0.1 M $LiClO_4$ as the electrolyte. Acetonitrile was purified by distillation from P_2O_5 under dry N_2 immediately prior to use. The peak oxidation potentials *vs* Ag/Ag^+ were converted to an SCE basis by adding 0.30 V.

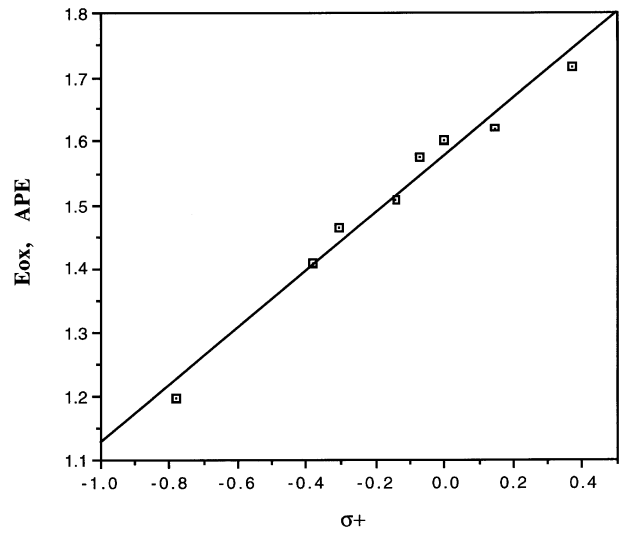


Figure 11. Plot of peak oxidation potentials (E_{OX}, V *vs* SCE) of aryl *cis*-propenyl ethers by DPV in acetonitrile *vs* σ^+. The correlation equation is $\Delta E_{OX} = 0.44717\ \sigma^+ + 1.2758$ ($r^2 = 0.976$)

Substrates. The aryl vinyl sulfides were prepared by a modification of a literature procedure[11] with the exception of phenyl vinyl sulfide, which was obtained from Aldrich.

General procedure for the synthesis of substituted aryl vinyl sulfides. An aryl Grignard reagent, from the reaction of an aryl bromide or iodide and excess Mg, was added, *via* a cannula, to a solution of 2-chloroethyl thiocyanate in THF at 0°C. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h, at which time the reaction was cooled to 0°C and a suspension of KOtBu (4–6-fold excess) in THF was carefully added. The reaction was refluxed for 1–2 h and checked by gas chromatography (GC). If GC analysis indicated that the reaction was not complete, then about two more equivalents of KOtBu

were added and reflux was continued for another hour. The reaction mixture was cooled to room temperature and then transferred to a separating funnel containing 100 ml of 10% $(NH_4)_2SO_4$, 100 ml of saturated NaCl and 200 ml of pentane. The aqueous layer was removed and the organic layer was then dried over $MgSO_4$ and the solvent removed at reduced pressure on a rotary evaporator. The residue was vacuum distilled at *ca* 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. 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: b.p.115–120 °C at 5 Torr; ^{1}H NMR, δ 3.76 (s, 3H), 5.1 (m, 2H), 6.43 (dd, 1H), 6.85 (d, 2H), 7.31 (d, 2H); ^{13}C NMR δ 55.1, 112.4, 114.7, 123.3, 133.5, 133.9, 159.5; low-resolution mass spectrometers (LRMS), *m/z* 166 (M^+), 151 (base), 135, 121, 107, 77; high-resolution (HR) MS, *m/z* calculated for $C_9H_{10}OS$ 166.0452, found 166.0453; E_p^{OX} = 1.097 V.

4-Methylphenyl vinyl sulfide. 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 of g 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: b.p. 95–105 °C at 5 Torr; ^{1}H NMR δ 2.3 (s, 3H), 5.2 (m, 2H), 6.45 (dd, 1H), 7.07 (d, 2H), 7.25 (d, 2H); ^{13}C NMR δ 21, 114.1, 129.8, 130, 131.2, 132.6, 137.3; LRMS, *m/z* 150 (M^+), 135 (base), 105, 91, 77; HRMS, *m/z* calculated for $C_9H_{10}S$ 150.0503, found 150.0498; E_p^{OX} = 1.267 V.

3-Methylphenyl vinyl sulfide. 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 25.5 g of KOtBu in 70 ml of THF. Distillation gave 10.864 g (72%) of product determined to be >98% pure by GC: b.p. 93–94 °C at 5 Torr; ^{1}H NMR, δ 2.32 (s, 3H), 5.3 (m, 2H), 6.5 (dd, 1H), 7.0 (m, 1H), 7.16 (m, 3H); 13C NMR, δ 21.2, 115.2, 127.4, 127.9, 128.9, 132, 133.9, 138.9; LRMS, *m/z* 150 (M^+), 135 (base), 105, 91, 77; HRMS, *m/z* calculated for $C_9H_{10}S$ 150.0503, found 150.0497; E_p^{ox} = 1.312 V.

4-Chlorophenyl vinyl sulfide. Using the above procedure, the Grignard reagent from 4-chloroiodobenzene (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: b.p. 105–110 °C at 5 Torr; 1H NMR, δ 5.38 (m, 2H), 6.45 (dd, 1H), 7.28 (s, 4H); ^{13}C NMR, δ 116.2, 129.2, 131.6, 132.4, 132.6; LRMS, *m/z* 170 (M^+), 135 (base), 108, 91, 75; HRMS, *m/z* calculated for C_9H_6ClS (M−H) 169.9947, found 169.9958; E_p^{OX} = 1.392 V.

3-Chlorophenyl vinyl sulfide. Using the above procedure, the Grignard reagent from 3-chloroiodobenzene (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 and required additional KOtBu (10 g). Distillation gave 4.098 g (58.7%) of product determined to be >96% pure by GC: b.p. 105–110 °C at 5 Torr; ^{1}H NMR, δ 5.4 (m, 2H), 6.45 (dd, 1H), 7.18 (s, 3H), 7.33 (s, 1H); ^{13}C NMR, δ 117.5, 126.9, 127.8, 129.3, 130, 130.4, 133.5, 136.7; LRMS, *m/z* 170 (M^+), 135 (base), 108, 91, 75; HRMS, *m/z* calculated for C_9H_6ClS (M + H) 171.0035, found 171.0034; E_p^{OX} = 1.467 V.

4-Trifluoromethylphenyl vinyl sulfide. 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: b.p. 80–83 °C at 5 Torr; ^{1}H NMR, δ 5.52 (m, 2H), 6.51 (dd, 1H), 7.38 (d, 2H), 7.55 (d, 2H); ^{13}C NMR, δ 119, 125.8, 125.9, 128.7, 129.5, 140.1; LRMS, *m/z* 204 (M^+), 183, 159, 135 (base), 91, 69; HRMS, *m/z* calculated for $C_9H_7F_3S$ 204.0221; found 204.0215; E_p^{OX} = 1.604 V.

3,5-Dichlorophenyl vinyl sulfide. 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: b.p. 110–115 °C at 3 Torr; ^{1}H NMR, δ 5.5 (m, 2H), 6.48 (dd, 1H), 7.18 (s, 3H); ^{13}C NMR, δ 119.6, 126.6, 126.9, 129.1, 135.3, 138.5; LRMS, *m/z* 204 (M^+), 169, 134 (base); HRMS, *m/z* calculated for $C_8H_5Cl_2S$ (M−H) 203.9567; found 203.9565; E_p^{OX} = 1.612 V.

4-(Methylthio)phenyl vinyl sulfide. First, 9.62 g of thioanisole (77.4 mmol) in 60 ml of pentane were converted into 4-bromothioanisole by the slow addition of a solution of 12.4 g (mmol) of Br_2 in 10 ml of pentane at room temperature. After 30 min., the solvent was removed and the crude product was adsorbed on 20 g of

basic alumina and placed on top of 50 g of basic alumina. The product was flashed off the column using hexane – EtOAc (9:1). After solvent removal, 14.3 g (84.7%) of 4-bromothioanisole was isolated. GC analysis of the crude product showed it was 93% pure and it was used without further purification: LRMS, *m/z* 204 (M^+), 202 (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: b.p. 100–110 °C at 1.5 Torr; ^{1}H NMR, δ 2.4 (s, 3H), 5.25 (m, 2H), 6.45 (dd, 1H), 7.11 (d, 2H), 7.25 (d, 2H); ^{13}C NMR, δ 15.8, 114.9, 127.2, 130.1, 131.7, 132.3, 138.3; LRMS, *m/z* 182 (M^+), 167, 135 (base), 123, 108, 91; HRMS, *m/z* calculated for $C_9H_{11}S_2$ (M+H) 183.0302; found 183.0296; E_p^{OX} = 1.104 V.

Synthesis and characterization of aryl cis-propenyl ethers. The latter substrates were prepared by the base (potassium *tert*-butoxide–DMSO) catalyzed isomerization of appropriate allyl aryl ethers.[12] The corresponding allyl ethers were obtained by reaction of the appropriate sodium aryloxide with allyl bromide in refluxing in ethanol. The crude allyl aryl ethers were isomerized without further purification.

Phenyl propenyl ether. Found to be 95% pure by GC: b.p. 25–26 °C at 1 Torr; ^{1}H NMR, δ 1.7 (dd, 3H), 4.8 (m, 1H), 6.3 (m, 1H), 6.9 (m, 3H), 7.2 (m, 2H); ^{13}C NMR, δ 9.2, 107.1, 116.0, 122.2, 129.4, 140.8, 157.5; LRMS, *m/z* 135 (M + H) (base), 119, 105, 95; HRMS, *m/z* calculated for $C_9H_{11}O$ 135.0810; found 183.0819.

4-Bromophenyl propenyl ether. Found to be 96% pure by GC: b.p. 72–74 °C at 0.3 Torr; ^{1}H NMR, δ 1.67 (dd, 3H), 4.8 (m, 1H), 6.2 (m, 1H), 6.7 (m, 2H), 7.3 (m, 2H); 13C NMR, δ 9.4, 108.1, 114.7, 117.7, 132.3, 140.3, 156.5; LRMS, *m/z* 213 (M + H) (base), 162, 134; HRMS, *m/z* calculated for $C_9H_{11}OBr$ 212.9915; found 212.9910.

3-Chlorophenyl propenyl ether. Found to be 98% pure by GC: b.p. 50–51 °C at 1 Torr; ^{1}H NMR, δ 1.6 (dd, 3H), 4.8 (m, 1H), 6.2 (m, 1H), 68 (m, 1H), 6.9 (m, 1H), 7.1 (m, 2H); ^{13}C NMR, δ 9.4, 108.7, 114.4, 116.6, 122.5, 130.3, 135.0, 140.2, 158.2; LRMS, *m/z* 169 (M + H) (base), 155, 149, 145, 141, 129, 125; HRMS, *m/z* calculated for $C_9H_{11}OCl$ 169.0420; found 169.0426.

3,4-Dimethylphenyl propenyl ether. Found to be 96% pure by GC: b.p. 49–50 °C at 2 Torr; ^{1}H NMR, δ 1.7 (dd, 3H), 2.1 (d, 6H), 4.7 (m, 1H), 6.28 (m, 1H), 6.7 (m, 2H), 6.9 (d, 1H); ^{13}C NMR, δ 9.4, 18.8, 19.8, 106.3, 113.4, 117.7, 140.3, 130.5, 137.8, 141.6, 155.9; LRMS, *m/z* 163 (M + H) (base), 147, 133, 123, 107, 91; HRMS, *m/z* calculated for $C_{11}H_{15}O$ 163.1123; found 163.1130.

3,5-Dimethylphenyl propenyl ether. Found to be 94% pure by GC: b.p. 59–60 °C at 1 Torr; ^{1}H NMR, δ 1.68 (dd, 3H), 2.2 (s, 6H), 4.7 (m, 1H), 6.3 (m, 1H), 6.5 (s, 3H); ^{13}C NMR, δ 9.4, 21.3, 106.7, 114.0, 124.2, 139.3, 141.3, 157.7; LRMS, *m/z* 162 (base), 147, 123; HRMS, *m/z* calculated for $C_{11}H_{15}O$ 163.1123; found 163.1128.

3-Methoxylphenyl propenyl ether. Found to be 96% pure by GC: b.p. 52–53 °C at 2 Torr; ^{1}H NMR, δ 1.7 (dd, 3H), 3.66 (s, 3H), 4.8 (m, 1H), 6.3 (m, 1H), 6.5 (m, 3H), 7.1 (m, 1H); ^{13}C NMR, δ 9.4, 55.1, 102.5, 107.4, 108.3, 130.1, 140.9, 158.8, 161.1.1; LRMS, *m/z* 164 (base), 149, 135, 125; HRMS, *m/z* calculated for $C_{10}H_{13}O_2$ 165.0916; found 165.0914.

4-Methoxylphenyl propenyl ether. Found to be 97% pure by GC: b.p. 54–56 °C at 2 Torr; ^{1}H NMR, δ 1.7 (dd, 3H), 3.6 (s, 3H), 4.7 (m, 1H), 6.2 (m, 1H), 6.7 (m, 3H), 7.1 (t, 1H); ^{13}C NMR, δ 9.4, 55.4, 106.0, 114.7, 117.4, 142.1, 151.8, 155.2; LRMS, *m/z* 164 (base); HRMS, *m/z* calculated for $C_{10}H_{13}O_2$ 165.0916; found 165.0907.

3-Methylphenyl propenyl ether. Found to be 95% pure by GC: b.p. 43–45 °C at 2 Torr; ^{1}H NMR, δ 1.7 (dd, 3H), 2.25 (s, 3H), 4.78 (m, 1H), 6.3 (m, 1H), 6.7 (m, 3H), 7.1 (t, 1H); ^{13}C NMR, δ 9.4, 21.3, 106.9, 113.2, 117.0, 123.2, 129.3, 139.6, 141.1. 157.7; LRMS, *m/z* 149 (M + H) (base), 133, 121, 109, 57; HRMS, *m/z* calculated for $C_{10}H_{13}O$ 149.0966; found 149.0961.

4-Methylphenyl propenyl ether. Found to be 96% pure by GC: b.p. 40–42 °C at 1 Torr; ^{1}H NMR, δ 1.7 (dd, 3H), 2.2 (s, 3H), 47 (m, 1H), 6.3 (m, 1H), 6.8 (d, 2H); 13C NMR, δ 9.4, 20.5, 106.5, 116.1, 130.1, 131.6, 141.5, 155.7; LRMS, *m/z* 148 (base), 133, 119, 107; HRMS, *m/z* calculated for $C_{11}H_{13}O$ 149.0966; found 149.0961.

4-Biphenyl propenyl ether. Found to be 99% pure by GC: m.p. 80–81 °C (recrystallized from hexane); ^{1}H NMR, δ 1.7 (dd, 3H), 4.9 (m, 1H), 64 (m, 1H), 7.0 (d, 2H), 7.2-7.4 (m, 3H), 7.5 (m, 4H); ^{13}C NMR, δ 9.4, 107.7, 116.4, 126.8, 126.9, 128.2, 128.7, 135.4, 140.6, 140.8, 157.0; LRMS, *m/z* 211 (M + H) (base), 171; HRMS, *m/z* calculated for $C_{15}H_{15}O$ 211.1123; found 211.1118.

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REFERENCES

1. E. M. Kosower, in *Progress in Physical Organic Chemistry*, edited by S.G. Cohen, A. Streitweiser, Jr, and R.W. Taft. pp. 122–124. Interscience, New York (1965).
2. G. A. Mirafzal, T. Kim, J. Liu and N. L. Bauld. *J. Am. Chem. Soc.* **114**, 10968–10969 (1992); T. Kim, G. A. Mirafzal, J. Liu and N. L. Bauld. *J. Am. Chem. Soc.* **115**, 7653–7664 (1993); T. Kim, G. A. Mirafzal and N. L. Bauld. *Tetrahedron Lett.* **34**, 7201–7204 (1993).
3. For example, T. Lowry and K. S. Richardson. *Mechanism and Theory in Organic Chemistry*, p. 150. Harper and Row, New York (1987).
4. C. Hansch, A. Leo and R. W. Taft. *Chem Rev.* **91**, 165–195 (1991).
5. D. P. Shoemaker, C. W. Garland and J. W. Nibler. *Experiments in Physical Chemistry*, pp. 811–820. McGraw-Hill, New York (1989).
6. T. Fueno, I. Matsumura, T. Okuyama and J. Furukawa. *Bull. Chem. Soc. Jpn.* **41**, 818–823 (1968).
7. R. A. McClelland. *Can. J. Chem.* **55**, 548–551 (1977).
8. M. Hojo, R. Masude, Y. Kamitori and E. Okada. *J. Am. Chem. Soc.* **56**, 1975–1976 (1991).
9. R. A. McClelland and M. Leung. *J. Org. Chem.* **45**, 187–189 (1980).
10. B. N. Solomonov, I. A. Arkhiriea and A. I. Konovalov. *Zh. Org. Khim.* **16**, 1666–1669, 1670–1674 (1980).
11. W. Verboom, J. Meuer and L. Brandsma. *Synthesis* 577 (1978).
12. C. C. Price and W. H. Snyder. *J. Am. Chem. Soc.* **83**, 1773 (1961). T. J. Prosser. *J. Am. Chem. Soc.* **83**, 1701–1704 (1961).

