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A Comparison of Substituent Field Effects on the Regiochemistry of the Ene Reactions of Allylic Sulfides and Ethers.

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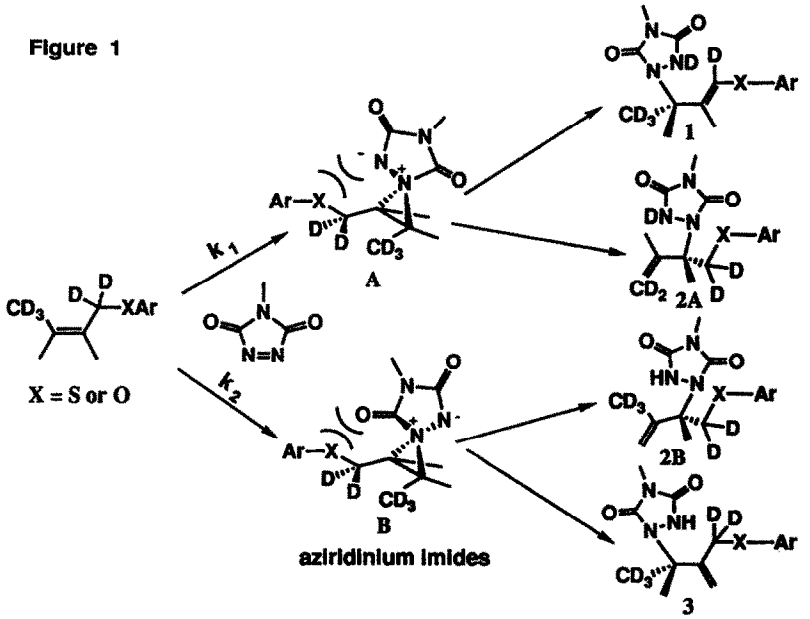
Abstract: The reactions of 4-methyl-1,2,4-triazolinedione with allylic ethers and sulfides have been examined. The different responses of the regiochemistry in the two reaction series to changes in the electronic character of the substituents is attributed to the difference in the C-S (1.82 Å) and C-O (1.43 Å) bond lengths and/or the larger van der Waals radius of sulfur in comparison to oxygen.

We have recently communicated evidence that the magnitude of the electronic field surrounding an allylic sulfur atom influences the regiochemical outcome of the ene reaction (Figure 1).[1] We now report the full details of that study and new data which demonstrates that the electrostatic field surrounding an oxygen atom can also influence reaction regiochemistry but with dramatically different results.

Figure 1



We have chosen 4-methyl-1,2,4-triazolinedione (MTAD) as the enophile for this study as a result of extensive experimental work which demonstrated that a configurationally stable aziridinium imide (AZI) intermediate is formed irreversibly in these reactions.[2,3] Structural constraints in the AZI's (Figure 1) dictate that **A** can only collapse to **1** and **2A** and that **B** can only collapse to **2B** and **3**. Consequently as a result of the experimentally demonstrated inability of **A** and **B** to interconvert[4-6] the values of ([**1**] + [**2A**]) and ([**2B**] + [**3**]) are a measure of the concentrations of the AZI diastereomers. The changes in these values as a function of substituent are therefore a measure of the relative importance of electrostatic effects during the formations of **A** and **B** and the changes in the ratios [**1**]/[**2A**] and [**3**]/[**2B**] are a measure of the relative importance of electrostatic field effects during their decompositions.

The yields of the products formed in the reactions of the deuterated allylic ethers are compared in Table 1 to similar data collected for the allylic sulfides. The regiochemical preference in the reactions of the ethers is for the formation of **2A/2B** (65% - 78%) in contrast to the allylic sulfides where **3** (46% - 78%) is the major product.

Table 1. Product Ratios in the Reactions of Allylic Sulfides and Ethers with MTAD.[a,b]

			%	
X	**Ar**	**1**	**2A/2B**	**3**
O	pNO_2Ph-	12(13)	37/41(77)	10(10)
O	pClPh-	15(14)	35/40(76)	10(10)
O	Ph-	17(18)	30/40(69)	13(13)
O	pMeOPh-	21(26)	25/40(59)	14(15)
S	pNO_2Ph-	17	13/24	46
S	pClPh-	14	8/17	61
S	Ph-	11	6/12	71
S	pMePh-	11	5/10	74
S	pMeOPh-	9	4/9	78

a. Product ratios were determined from the cutting and weighing of appropriate expanded peaks in the proton NMR of the crude reaction mixture. The data represents of average of two runs and are good to ±2%. b. Data in parenthesis collected in an identical manner to the deuterated compounds for the perhydro analogues.

The mechanistically revealing product sums and ratios for both reaction series are given in Table 2. In the sulfide series [**1** + **2A**] decreases and [**3** + **2B**] increases with increasing electron donating ability of the substituent. This demonstrates that the developing sulfur-nitrogen interaction in **A** is more destabilizing than the developing sulfur-carbonyl oxygen interaction in **B** during the formations of the AZI intermediates. However, it is the sulfur-carbonyl oxygen interaction which is more destabilizing during the decompositions of the AZI's as revealed by the much larger change in [**3**]/[**2B**] in comparison to [**1**]/[**2A**].

These results are consistent with the mechanism depicted in Figure 2. **A'** and **B'** represent the two parallel approaches of the reactants which minimize steric and maximize frontier orbital interaction. In these approach geometries the sulfur-nitrogen distance in **A'** is shorter than the sulfur-carbonyl oxygen distance in

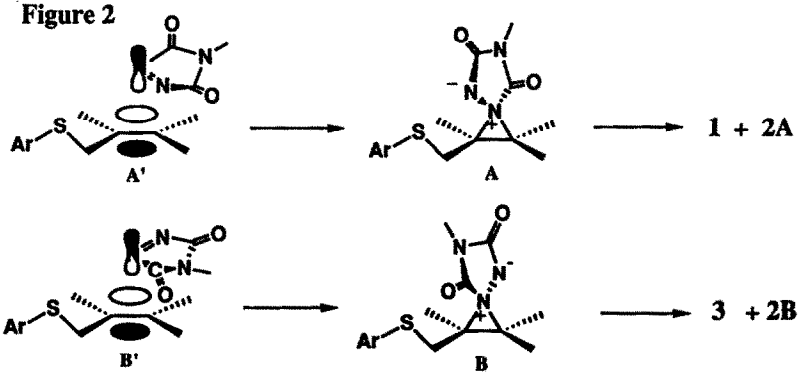
B'. To the extent that these geometries mimic the geometries in the transitions states for AZI formation it is not surprizing that the sulfur-nitrogen interaction plays the dominant role. However, the sulfur-carbonyl oxygen distance in the perpendicular geometry of AZI B is smaller and the sulfur-nitrogen distance in AZI A is approximately the same as in the parallel approach geometry. The dominance of the sulfur-carbonyl interaction late in the reaction is therefore consistent with a transition state for decomposition which look very much like the AZI. The absolute increases in [1] and [3] with increasing electron donating ability of the substituents (Table 1) reflects elongation of the hashed bonds in A(X = O) and B(X = S, O) in order to circumvent the destabilizing electrostatic interaction.

Table 2. Product Sums and Ratios in the Reactions of Allylic Sulfides and Ethers with MTAD.

ArX	[1 + 2A]	[3 + 2B]	[1]/[2A]	[3]/[2B]
pNO_2PhS	30	70	1.31	1.92
pClPhS	22	78	1.75	3.59
pHPhS	17	83	1.83	5.92
pMePhS	16	84	2.2	7.4
pMeOPhS	13	87	2.25	8.67
pNO_2PhO	49	51	0.32	0.24
pClPhO	50	50	0.43	0.25
pHPhO	47	53	0.57	0.33
pMeOPhO	46	54	0.84	0.35

In comparison to the sulfides the ratios [1 + 2A] and [3 + 2B] observed in the reactions of the ethers (Table 2) are insensitive to changes in substituent. This reveals a lack of electrostatic interaction between the allylic oxygen and the nitrogen or carbonyl oxygen in the parallel-like transition states, A' and B', for the formation of the AZI's. This insensitivity to electrostatic effects is most conveniently rationalized in terms of the proximity of the interacting groups in the transition states for reaction; a C-O bond is considerably shorter (1.43 Å) than a C-S bond (1.82 Å). In addition, the near equivalence of [1 + 2A] and [3 + 2B] suggests that steric interactions as well as electrostatic bias in the two parallel approach geometries are nearly identical.

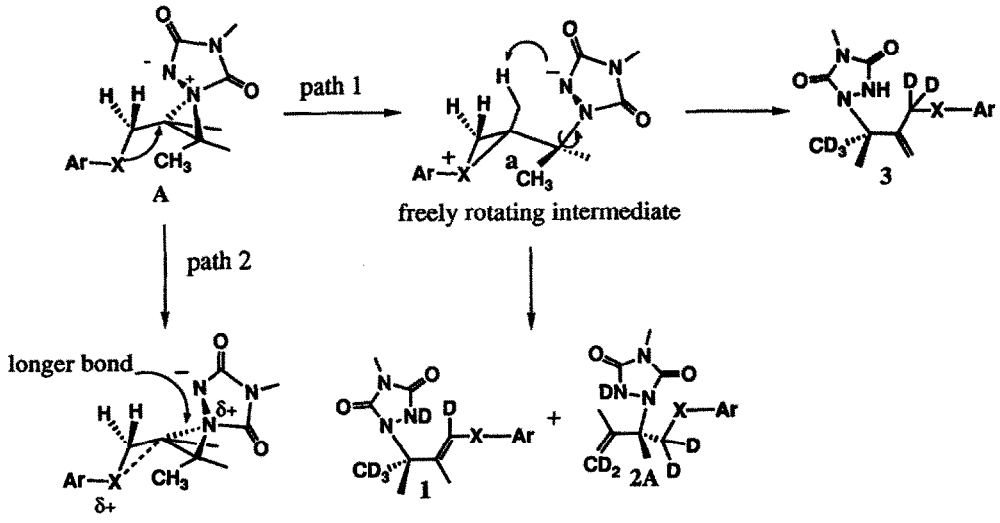
Figure 2



The ratios **[1]/[2A]** and **[3]/[2B]** are also very different in the two reaction series. It is **[1]/[2A]** in the reactions of the ethers rather than **[3]/[2B]** which is the most sensitive to changes in substituent. This suggests that in the decomposition of the AZI's formed in the reactions of the allylic ethers that it is the oxygen-nitrogen rather than the oxygen-carbonyl oxygen interaction which is most destabilizing. Examination of molecular models indicates that the origin of this phenomenon also lies in the shorter C-O in comparison to C-S bond. Decreasing the length of the C-X bond (Figure 1) slightly decreases the through space distance between the interacting groups in AZI **A** but increases the interaction distance in AZI **B**. Consistent with a diminished electrostatic effect in the ethers is the observation that the major interaction (**[1]/[2A]** in the ethers and **[3]/[2B]** in the sulfides) changes by a factor of 4.5 in the sulfides but by only of factor of 2.6 in the ethers.

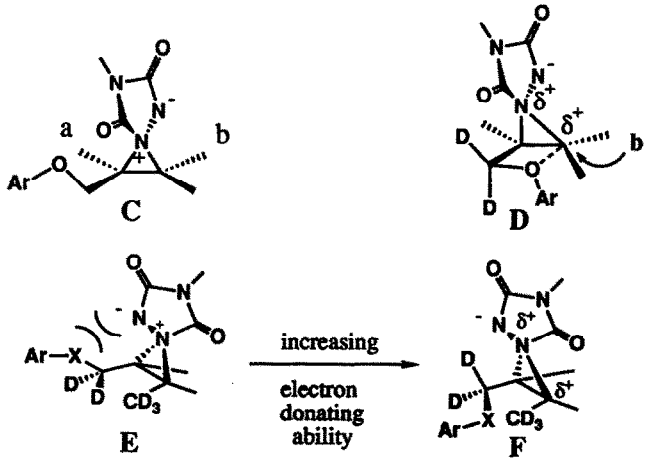
We have previously pointed out that an anchimerically assisted opening of the aziridinium imide intermediate (path 1 in Figure 3) is incompatible with the absence of any induced isotope effect for the formation of **3**.[1] The population of the freely rotating intermediate implies that replacement of methyl **a** with a CD_3 group would change the branching ratio **[3]/[1 + 2A]** by increasing the formation of **3**; contrary to what is experimentally observed. This result cannot rule out the possibility that anchimerically assisted weakening of the aziridinium imide bond without population of a freely rotating intermediate (path 2 in Figure 3) might facilitate a Cope-like *syn* elimination reaction. The weakening of the aziridinium imide bond in path 2 is more advanced for electron donating than electron withdrawing substituents and provides a convenient explanation for the increases in the **[1]/[2A]** and **[3]/[2B]** ratios with increasing electron density on the heteroatom X. This mechanism, however, incorrectly predicts that the magnitude of the substituent effect on both **[1]/[2A]** and **[3]/[2B]** should be nearly identical.

Figure 3



The ratios [1]/[2A] and [3]/[2B] are also both less than one in the allylic ethers but greater than one in the allylic sulfides. On both steric and electrostatic grounds one would have anticipated that the ratios would have been greater than one in both reaction series. (This is especially true for the ratio [3]/[2B] where no statistical factor needs be taken into account because it involves competition between loss of hydrogen from two methyl groups.) In the absence of destabilizing electrostatic control some other structural feature is clearly responsible for the preferential opening of the solid three membered ring bonds in the AZI intermediates derived from the allylic ethers leading to **2A** and **2B** rather than the hashed bonds leading to **1** and **3** (Figure 1).

Likely candidates for the other structural feature are: (i) a small activation barrier for hydrogen abstraction as a result of a lower rotational barrier for the methyl trans in comparison to the methyl geminal to the phenoxy substituent.[7] Recently Orfanopoulos has criticized the use of rotational barrier magnitudes to predict ene regiochemistry claiming that the barriers are irrelevant.[8] Unfortunately, their argument is flawed since they did not compare the effect of barrier heights on two methyl groups equally accessible to the abstracting heteroatom. Rotational barriers do correctly predict the site of hydrogen abstraction from competing methyl groups in all but the most sterically hindered cases. If the Curtin-Hammett principle applies (i.e. if rotations of the methyl groups are much faster than hydrogen abstraction) a difference of only 0.8kcal/mol in the rotational barriers is required to explain the 4/1 preference for abstraction of hydrogen from methyl b in aziridinium imide **C**. (ii) the strengths of the competing carbon-hydrogen bonds. The strengths of the competing carbon-hydrogen bonds are difficult to estimate and as a consequence we cannot at this time evaluate their effect on the reaction regiochemistry. (iii) an ether rotomer population about the CD_2-AZI bond which would allow electrostatic stabilization of a partial positive charge at carbon **b** as shown in aziridinium imide **D**. An electrostatic induced shift in the rotomer population from **E** to **F** as the electron donating ability of the substituent is increased accompanied by the interaction depicted in **D** would provide an explanation for the substituent induced changes in [1]/[2A] and [3]/[2B] in both the sulfides and ethers, and (iv) the stability of the resulting olefin. Preliminary molecular mechanics results do appear to predict that **2B** is more stable than **3**. Additional experimental and computational studies, however, will be necessary in order to determine the importance of each of these factors.



In contrast to the absence of a specific through space electrostatic interaction which influences the reaction regiochemistry, a through bond (possibly hyperconjugative) inductive effect which influences the rate of the reactions of the allylic ethers is clearly discernible in the kinetic data presented in Table 3. In both the allylic ether and sulfide series electron donating substituents increase the rate of the reaction with the enophile. This is consistent with kinetic data in other ene reactions which have established the electrophilic character of triazolinediones.[9]

Table 3. Rate Constants for the Reactions of Allylic Ethers (X = O) and Sulfides (X = S) with MTAD.

X	Ar	$k(M^{-1}s^{-1}) \times 10^{2a}$
S	pNO_2Ph-	9.9
S	pMeOPh-	32.9
O	pNO_2Ph-	3.9
O	pMeOPh-	12.4

a. Measured in acetone by following the disappearance of the triazolinedione at 526nm under pseudo first order conditions.

In recent years a new appreciation of the importance of electrostatic effects in organic reactions has developed.[10-16] These results demonstrate how subtle changes in the magnitude of the interaction can lead to dramatic shifts in product composition.

Experimental Section

Chromatographic purifications of the deuterated allylic sulfides and ethers were carried out on a Harrison Research Model 7624T chromatotron using plates coated with EM science 7749 silica gel $60PF_{254}$. Proton and carbon NMR were obtained either on a JEOL GX 270 or 400MHz NMR and are referenced in ppm to TMS. The NMR spectra of the ether allylic urazole products were assigned by comparison to the analogous sulfide and with the aid of exhaustive single frequency decoupling experiments. The deuterated allylic sulfides were synthesized as previously reported.[17a] Acetone-d_6, and $LiAlD_4$ were obtained from Aldrich and used without purification. 4-Methyl-1,2,4-triazoline-3,5-dione was synthesized from 4-methylurazole by the method of Cookson.[18]

Allylic ethers. In a 50 ml three-necked flask containing 10 ml of absolute ethanol, 101 mg of sodium (4.4 mmol) was added in small portions under an argon atmosphere. After complete disappearance of the sodium, one equivalent of substituted phenol was immediately added and the mixture stirred for one hour at room temperature. 1-Bromo-2,3-dimethyl-2-butene (570 mg, 3.7 mmol) was added dropwise and the resulting reaction mixture was stirred at 60-70 °C for three hours. The mixture was cooled down to room temperature and ethanol was removed under reduced pressure. The residue was dissolved in 20 ml of ethyl ether. The ether solution was washed with three 5 ml portions of saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. The ether was removed and the product was purified by chromatography.

2,3-dimethyl-2-butenyl p-nitrophenyl ether. solid, mp. 51-52.5 °C, yield 46.6%. IR(neat, NaCl window) v: 3040, 2990, 2923, 1592, 1512, 1341, 1298, 1257, 1171, 1111, 982, 845, 752 cm^{-1}. ^1H NMR(270 MHz, $CDCl_3$) δ 1.75(s, 6H), 1.78(s, 3H), 4.57(s, 2H), 6.94(d, J = 9.3 Hz, 2H), 8.18(d, J = 9.3 Hz, 2H). ^{13}C NMR(270 MHz, $CDCl_3$) δ 16.5(q, J = 126 Hz), 20.3(q, J = 126 Hz), 20.9(q, J = 127 Hz), 70.0(t, J = 143 Hz), 114.6(dd, J = 6, 164 Hz), 122.7(s), 125.8(dd, J = 4, 170 Hz), 132.3(s), 141.3(s), 164.3(s). GC-MS: 221($M^{+\cdot}$), 83($C_6H_{11}^+$, 100%), 67, 55. HRMS: 221.1041($M^{+\cdot}$, 1.07%, calc. 221.1052, Dev. -5.01 ppm), 123.0318($M^{+\cdot}$ - $C_6H_{10}O$, 1.82%), 83.0862($C_6H_{11}^+$, 100%).

2,3-Dimethyl-2-butenyl p-chlorophenyl ether. oily liquid, yield 50.0%. IR(neat, NaCl window) v: 3040, 2990, 2922, 1596, 1490, 1285, 1236, 1167, 1093, 997, 823 cm^{-1}. ^1H NMR(270 MHz, acetone-d_6) δ 1.71(s, 3H), 1.72(s, 3H), 1.76 (s, 3H), 4.52(s, 2H), 6.93(d, J = 9.2 Hz, 2H), 7.26(d, J = 9.3 Hz, 2H). ^{13}C NMR($CDCl_3$) δ 16.6(q, J = 126 Hz), 20.3(q, J = 126 Hz), 20.9(q, J = 126 Hz), 69.5(t, J = 146 Hz), 116.0(d, J = 165 Hz), 123.6(s), 125.4 (s), 129.2(d, J = 165 Hz), 131.3(s), 157.8(s). GC-MS: 212 & 210(M+ 2, M, 1:3), 169, 167, 141, 130 & 128(1:3, 100%), 83, 77. HRMS: 212.0781($C_{12}H_{15}O^{37}Cl^{+\cdot}$, 1.60%, calc. 210.0782, Dev. -0.39 ppm), 210.0817($C_{12}H_{15}O^{35}Cl^{+\cdot}$, 5.75%, calc. 212.0782, Dev. 2.75 ppm), 128.0033($C_6H_5O^{35}Cl^{+\cdot}$, 100%), 83.0857(C_6H_{11}+, 68.7%)

2,3-Dimethyl-2-butenyl phenyl ether. oily liquid, b.p. 115 °C/15 mmHg, yield, 66.6%. IR(neat, NaCl window) v: 3040, 2990, 2919, 1599, 1494, 1373, 1299, 1236, 1171, 1077, 1029, 1006, 827, 753, 690 cm^{-1}. ^1H NMR(270 MHz, $CDCl_3$) δ 1.68(s, 3H), 1.72(s, 6H), 4.42(s, 2H), 6.84-6.89(m, 3H), 7.18-7.21(m, 2H). ^{13}C NMR(270 MHz, $CDCl_3$) δ 16.7(q, J = 126 Hz), 20.2(q, J = 126 Hz), 20.9(q, J = 125 Hz), 69.0(t, J = 142 Hz), 114.6(dt, J = 7, 158 Hz), 120.4(dt, J = 7, 161 Hz), 123.9(s), 129.3(dd, J = 9, 158 Hz), 131.0(s), 159.2(s). GC-MS: 176($M^{+\cdot}$), 94($C_6H_5OH^{+\cdot}$, 100%), 83($C_6H_{11}^+$), 67, 55. HRMS: 176.1197($M^{+\cdot}$, 7.63%, calc. 176.1201, Dev. -2.57 ppm), 161.0968($M^{+\cdot}$ - CH_3, 0.46%), 94.0418($C_6H_6O^{+\cdot}$, 100%), 83.0859($C_6H_{11}^+$, 39.49%).

2,3-Dimethyl-2-butenyl p-methoxyphenyl ether. oily liquid, yield 59.7%. IR(neat, NaCl window) v: 3042, 2990, 2923, 1591, 1507, 1465, 1374, 1226, 1181, 1106, 1040, 1003, 825, 765 cm^{-1}. ^1H NMR(270 MHz, $CDCl_3$) δ 1.72(s, 3H), 1.75(s, 6H), 3.75(s, 3H), 4.42(s, 2H), 6.83 (m, 4H). ^{13}C NMR(270 MHz, $CDCl_3$) δ 16.6(q, J = 126 Hz), 20.1(q, J = 126 Hz), 20.8(q, J = 126 Hz), 55.5(q, J = 144 Hz), 69.7(t, J = 142 Hz), 114.5(d, J = 114 Hz), 115.6(d, J = 114 Hz), 124.0(s), 130.6(s), 153.3(s), 153.7(s). GC-MS: 206($M^{+\cdot}$), 124($pMeOC_6H_4OH^{+\cdot}$, 100%), 109, 95, 83, 55. HRMS: 206.1300($M^{+\cdot}$, 1.27%, calc. 206.1307, Dev. -3.53 ppm), 124.0526($C_7H_8O_2^+$, 100%), 109.0285($C_6H_5O_2^{+\cdot}$, 31.39%), 83.0856($C_6H_{11}^+$, 13.44%).

Deuterated Allylic ethers. The allylic ethers were synthesized by the addition of one equivalent of a sodium thiophenoxide to Z-1,1,4,4,4-d_5-1-bromo-2,3-dimethyl-2-butene[17] dissolved in 20 ml of anhydrous ethanol. The reaction mixtures were heated at 60 °C for 5 h followed by removal of ethanol at reduce pressure. Diethylether was added to the residues and the resulting solutions washed with three 5ml portions of saturated NaCl and dried with $MgSO_4$. The diethylether was removed under reduce pressure to give the deuterated allylic ethers. Ar = p-NO_2Ph-; ^1H NMR (acetone-d_6) δ 1.73(s, 3H), 1.75(s, 3H), 7.11(d, J = 9 Hz, 2H), 8.18(d, J = 9 Hz, 2H). Ar = p-ClPh; ^1H NMR (acetone-d_6) δ 1.70(s, 3H), 1.72(s, 3H), 6.91(d, J = 9 Hz, 2H), 7.24(d, J = 9 Hz, 2H). Ar = Ph-; ^1H NMR (acetone-d_6) δ 1.71(s, 3H), 1.73(s, 3H), 6.90(m, 3H), 7.24(m, 2H), Ar = pMeOPh-; ^1H NMR (acetone-d_6) δ 1.69(s, 3H), 1.72(s, 3H), 3.72(s, 3H), 6.79-6.87(m, 4H).

Ene Reactions of Allylic Ethers. The allylic ethers were allowed to react with one equivalent of MTAD (2 x 10^{-2} M) in acetone-d_6 at -78 °C in 5 mm NMR tubes. The progress of the reactions was monitored by the disappearance of the characteristic red color of MTAD and by ^{1}H NMR. The relative yields of the products (Table 1) were determined by ^{1}H NMR integration of the vinyl hydrogens between 4 and 7 ppm and by cutting and weighing these peaks from expanded portions of the NMR spectra. **1** Ar = p-NO_2Ph-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.60(s, 6H), 1.78(s, 3H), 2.90(s, 3H), 6.78(q, long range J = 1.3 Hz, 1H), 7.29(d, J = 9.3 Hz, 2H), 8.23(d, J = 9.3 Hz, 2H), 8.85(bs, 1H). Ar = p-ClPh-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.59(s, 6H), 1.75(s, 3H), 2.90(s, 3H), 6.61(q, long range small J, 1H), 7.09(d, J = 8.8 Hz, 2H), 7.33(d, J = 8.8 Hz, 2H), 8.80(bs, 1H). Ar = Ph-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.60(s, 6H), 1.76(s, 3H), 2.91(s, 3H), 6.62(q, long range J = 1.3 Hz, 1H), 7.05(d, J = 8.4 Hz, 3H), 7.33(d, J = 8.4 Hz, 2H), 8.80(bs, 1H). Ar = p-MeOPh-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.59(s, 6H), 1.75(s, 3H), 2.91(s, 3H), 3.75(s, 3H), 6.53(q, long range J = 1.3 Hz, 1H), 6.86-6.98(m, 4H), 8.80(bs, 1H). **2** Ar = p-NO_2Ph-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.75(s, 3H), 1.86(s, 3H), 2.91(s, 3H), 4.46(d, J = 9.6 Hz, 1H), 4.78(d, J = 9.6 Hz, 1H), 5.05(q, long range J = 1.3 Hz, 1H), 5.08(s, 1H), 7.17(d, J = 9.2 Hz, 2H), 8.20(d, J = 9.2 Hz, 2H), 8.85(bs, 1H). ^{13}C NMR (270 MHz, acetone-d_6) Measured in a mixture (13:77:10) of **1**, **2**, and **3**. The minor components **1**, and **3** gave only small peaks which allowed unambiguous assignment of the ^{13}C chemical shifts to **2**. δ 20.5(q, J = 126 Hz), 21.9(q, J = 126 Hz), 25.8(q, J = 141 Hz), 67.5(s), 73.1(t, J = 145 Hz), 114.9(t, J = 154 Hz), 116.7(dd, J = 6, 165 Hz), 127.4(dd, J = 6, 168 Hz) 143.4(s), 146.2(s), 156.4(s), 165.4(s). Ar = p-ClPh-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.72(s, 3H), 1.84(s, 3H), 2.90(s, 3H), 4.28(d, J = 9.2 Hz, 1H), 4.58(d, J = 9.2 Hz, 1H), 5.02(bd probably q, 1H), 5.05(s, 1H), 6.97(d, J = 9.2 Hz, 2H), 7.28(d, J = 9.2 Hz, 2H), 8.80(bs, 1H). Ar = Ph-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.73(s, 3H), 1.85(s, 3H), 2.91(s, 3H), 4.28(d, J = 9.4 Hz, 1H), 4.57(d, J = 9.4 Hz, 1H), 5.03(bs, 1H), 5.06(s, 1H), 6.94(m, 3H), 7.26(m, 2H), 8.80(bs, 1H). Ar = p-MeOPh-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.71(s, 3H), 1.84(s, 3H), 2.91(s, 3H), 3.72(s, 3H), 4.21(d, J = 9.6 Hz, 1H), 4.50(d, J = 9.6 Hz, 1H), 5.01(bs, 1H), 5.04(s, 1H), 6.81-6.88(m, 4H), 8.80(bs, 1H). **3** Ar = p-NO_2Ph-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.61(s, 6H), 2.93(s, 3H), 4.89(s, 2H), 5.30(bt, 1H), 5.32(bs, 1H), 7.17(d, J = 9.2 Hz, 2H), 8.20(d, J = 9.2 Hz, 2H), 8.85(bs, 1H). Ar = p-ClPh-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.59(s, 6H), 2.91(s, 3H), 4.71(s, 2H), 5.29(bt, 1H), 5,31(bs, 1H), 6.96(d, J = 9.2 Hz, 2H), 7.28(d, J = 9.2 Hz, 2H), 8.80(bs, 1H). Ar = Ph-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.61(s, 6H), 2.92(s, 3H), 4.70(s, 2H), 5.28(s, 1H), 5.32(s, 1H), 6.94(m, 3H), 7.26(m, 2H), 8.80(bs, 1H). Ar = p-MeOPh-, X = O ^{1}H NMR (270 MHz, acetone-d_6) δ 1.59(s, 6H), 2.93(s, 3H), 3.72(s, 3H), 4.63(s, 2H), 5.26(bs, 1H), 5.30(bs, 1H), 6.81-6.88(m, 4H), 8.80(bs, 1H).

Ene Reactions of Deuterated Allylic Ethers. The ene reactions were run in 5 mm NMR tubes by addition of one equivalent of 4-methyl-1,2,4-triazolinedione (MTAD) to cold (-78 °C) acetone-d_6 solutions of the deuterated allylic sulfides and ethers. The red color of the triazolinedione was dissipated upon warmly slowly to room temperature. The product ratios were determined by cutting and weighing appropriate peaks from the proton NMR spectra. The NMR spectral assignments were made with the aid of single frequency decoupling experiments and by comparison to the analogous sulfides. **1** Ar = p-NO_2Ph-, X = O ^{1}H NMR (acetone-d_6) δ 1.60(s, 3H), 1.78(s, 3H), 2.91(s, 3H), 7.28(d, J = 9Hz, 2H), 8.22(d, J = 9 Hz, 2H), Ar = p-ClPh-, X = O ^{1}H NMR (acetone-d_6) δ 1.59(s, 3H), 1.75(s, 3H), 2.89(s, 3H), 7.10(d, J = 9 Hz, 2H), 7.29(d, J = 9Hz, 2H), Ar =

Ph-, X = O ^{1}H NMR (acetone-d_6) δ 1.58(s, 3H), 1.75(s, 3H), 2.89(s, 3H), 7.08(m, 3H), 7.28(m, 2H), Ar = p-MeOPh-, X = O ^{1}H NMR (acetone-d_6) δ 1.59(s, 3H), 1.74(s, 3H), 2.89(s, 3H), 3.75(s, 3H), 6.80-7.00(m, 4H). **2A** Ar = p-NO_2Ph-, X = O ^{1}H NMR (acetone-d_6) δ 1.75(s, 3H), 1.86(s, 3H), 2.91(s, 3H), 7.16(d, J = 9 Hz, 2H), 8.20(d, J = 9 Hz, 2H), Ar = p-ClPh-, X = O ^{1}H NMR (acetone-d_6) δ 1.75(s, 3H), 1.83(s, 3H), 2.90(s, 3H), 6.96(d, J = 9 Hz, 2H), 7.26(d, J = 9 Hz, 2H), Ar = Ph-, X = O ^{1}H NMR (acetone-d_6) δ 1.75(s, 3H), 1.83(s, 3H), 2.90(s, 3H), 6.94(m, 3H), 7.25(m, 2H), Ar = p-MeOPh-, X = O ^{1}H NMR (acetone-d_6) δ 1.71(s, 3H), 1.83(s, 3H), 2.89(s, 3H), 3.72(s, 3H), 6.80-6.87(m, 4H). **2B** Ar = p-NO_2Ph-, X = O ^{1}H NMR (acetone-d_6) δ 1.75(s, 3H), 2.91(s, 3H), 5.05(bs, 1H), 5.08(bs, 1H), 7.16(d, J = 9 Hz, 2H), 8.20(d, J = 9 Hz, 2H), 8.74-8.80(bs, 1H), Ar = p-ClPh-, X = O ^{1}H NMR (acetone-d_6) δ 1.75(s, 3H), 2.90(s, 3H), 5.02(bs, 1H), 5.05(bs, 1H), 6.96(d, J = 9 Hz, 2H), 7.26(d, J = 9Hz, 2H), 8.70-8.80(bs, 1H), Ar = Ph-, X = O ^{1}H NMR (acetone-d_6) δ 1.75(s, 3H), 2.90(s, 3H), 5.02(bs, 1H), 5.05(bs, 1H), 6.94(m, 3H), 7.25(m, 2H), 8.65-8.80(bs, 1H), Ar = p-MeOPh-, X = O ^{1}H NMR (acetone-d_6) δ 1.71(s, 3H), 2.89(s, 3H), 3.72(s, 3H), 5.01(bs, 1H), 5.03(bs, 1H), 6.80-6.87(m, 4H), 8.63-8.80(bs, 1H), **3** Ar = p-NO_2Ph-, X = O ^{1}H NMR (acetone-d_6) δ 1.62(s, 3H), 2.93(s, 3H), 5.30(bs, 1H), 5.33(bs, 1H), 7.16(d, J = 9 Hz, 2H), 8.20(d, J = 9 Hz, 2H), 8.74-8.80(bs, 1H), Ar = p-ClPh-, X = O ^{1}H NMR (acetone-d_6) δ 1.59(s, 3H), 2.92(s, 3H), 5.28(bs, 1H), 5.30(bs, 1H), 7.08(d, J = 9 Hz, 2H), 7.29(d, J = 9 Hz, 2H), 8.70-8.80(bs, 1H), Ar = Ph-, X = O ^{1}H NMR (acetone-d_6) δ 1.59(s, 3H), 2.91(s, 3H), 5.28(bs, 1H), 5.30(bs, 1H), 6.95(m, 3H), 7.25(m, 2H), 8.65-8.80(bs, 1H), Ar = p-MeOPh-, X = O ^{1}H NMR (acetone-d_6) δ 1.59(s, 3H), 2.91(s, 3H), 3.72(s, 3H), 5.26(bs, 1H), 5.20(bs, 1H), 6.80-6.87(m, 4H), 8.63-8.80(bs, 1H)

Rate Determinations. The rate constants for the reactions of the allylic sulfides and ethers in acetone which appear in Table 3 were determined by monitoring at room temperature the pseudo first order loss of the triazolinedione at 526 nm. These pseudo first order rate constants were determined at a minimum of five different concentrations of MTAD and were converted to the second order rate constants by plotting $k_{obs}(s^{-1})$ versus the concentration of MTAD used in that particular pseudo first order rate determination. The plots of k_{obs} versus [MTAD] had correlation coefficients of at least 0.99 in each case.

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