The Importance of Polar, Resonance, Steric and Solvent Effects in the Addition of Sulfonyl Radicals to Alkenes

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The radical chain addition of tosyl iodide to some alkenes has been studied. The reaction was carried out at room temperature under visible light, giving the usual high yields of β-iodo sulfones. These adducts were transformed into the corresponding unsaturated sulfones. Relative reactivities of the addition of the tosyl radical to alkenes were measured in acetonitrile, dichloromethane and carbon tetrachloride, the effect of the solvent being important only with polarized alkenes, such as vinyl and allyl cyanides, which are stabilized in solvents with greater π^* and AN parameters. The delocalization of the unpaired electron in the adduct radicals over the carbonyl and cyano groups is not important; the phenyl group is the only group that is able to affect the reactivity, increasing it notably. Polar and steric effects are dominant in all the other cases.

The participation of polar effects in the radical addition of arenesulfonyl halides to unsaturated compounds is well documented.[1] The study of the radical addition of several substituted benzenesulfonyl iodides ($Y{-}C_6H_4{-}SO_2I$) to substituted styrenes[1a] ($X{-}C_6H_4{-}CH{=}CH_2$) and substituted phenylacetylenes[1b] ($X{-}C_6H_4{-}C{\equiv}CH$) has shown the electrophilic character of arenesulfonyl radicals. Relative reactivities of addition correlate quite well with the Hammett σ constants, the correlations with σ^+ being better than with σ. The ρ values are small but significant (-0.50 to -0.93); sulfonyl radicals with electron-withdrawing substituents Y are more selective (greater ρ) and also more reactive. The relative reactivities and selectivities were rationalized[1b] on the grounds of an early transition state and frontier molecular orbital (FMO) theory.[2] Molecular orbital calculations also indicated that the addition of sulfonyl radicals to alkenes have reactant-like transition states.[3] The addition of methanesulfonyl and arensulfonyl radicals to various vinylic monomers was carried out by Takahara *et al.*[4] showing again the electrophilic character of sulfonyl radicals.

In the study of the cyclization of hex-5-enyl radicals produced by the addition of tosyl radicals to allyl acrylates and similar compounds[5] it was seen that the delocalization of the unpaired electron over the carbonyl group could have some importance, in that it could compensate for the polar effect of the carbonyl group. Relative reactivities of propyl (and butyl) acrylates and allyl propyl (and butyl) ethers were identical.

The importance of structure–reactivity relationships in sulfonyl radical chemistry is well illustrated in the work of Whitham,[6] which is based on the opposed 'philicity' of sulfonyl (electrophilic) and alkyl (nucleophilic) radicals.

In previous studies of the relative reactivities of addition of arenesulfonyl radicals to unsaturated compounds (styrenes and phenylacetylenes)[1a,b] the radical adducts (such as $X{-}C_6H_4{-}\dot{C}H{-}CH_2{-}SO_2Ar$) formed have the substituents X separated from the reaction site by the benzene ring. We report now the study of relative reactivities of addition of tosyl radicals ($Ts^{\bullet}$) to several alkenes with X closer to the double bond, $CH_2{=}CRX$; the effect of the solvent was also analysed.

Results and Discussion

Addition of Tosyl Iodide to some Alkenes.—The addition reactions were carried out at room temperature under sunlight or visible light for some minutes and the reaction products characterized by NMR and IR spectroscopies, GC–MS, elemental analysis and by transformation into dehydroiodinated derivatives.

The addition is regiospecific, the terminal carbon being preferred. Internal double bonds are also attacked. The results are summarized in Tables 1 and 2.

Effect of Substituents on the Rate of Addition.—Relative reactivities of the alkenes towards tosyl radicals were measured by competition experiments based on reactions (1) and (2), by using eqn. (3) where $[M^1]_0$, $[M^2]_0$ and $[M^1]$, $[M^2]$ are the initial and final concentrations of both alkenes in competition.

$$Ts^{\bullet} + M^1 \xrightarrow{k_1} \text{Radical adduct 1} \qquad (1)$$

$$Ts^{\bullet} + M^2 \xrightarrow{k_1} \text{Radical adduct 2} \qquad (2)$$

$$k_1/k_2 = (\log[M^1] - \log[M^1]_0)/(\log[M^2] - \log[M^2]_0) \qquad (3)$$

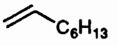
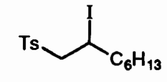
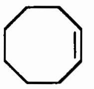
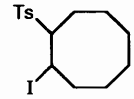
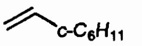
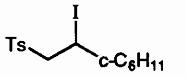
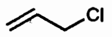
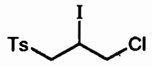
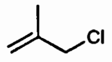
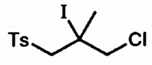
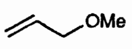
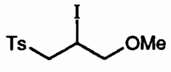
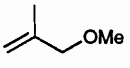
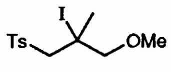
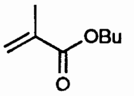
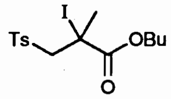
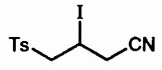
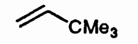
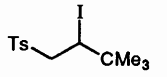
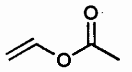
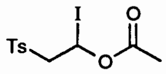
The alkenes were analysed by GC. This technique has been used several times by us[1] and its validity when applied to chain addition reactions with fast propagation steps was demonstrated by the results of Iino and Matsuda[4] and Gozdz and Maslak.[7] The results are summarized in Tables 3–5.

Table 3 shows that simple terminal alkenes, like oct-1-ene and hex-1-ene (entry 1), show similar reactivity towards tosyl radicals. 3,3-Dimethylbut-1-ene (entry 2) is less reactive than hex-1-ene (entry 1) and this shows the importance of the steric effects on the reactivity. The stronger donor effect of *tert*-butyl ($\sigma^* = -0.30$) as compared to butyl ($\sigma^* = -0.13$) is not great enough to cancel the retarding effect of the *tert*-butyl group ($E_s = -1.54$) as compared to the butyl group ($E_s = -0.39$).[8]

As expected, styrene (entry 4) is the most reactive of all the alkenes; this stabilizing effect of the phenyl group in the β-position is well known in radical reactions. Cyclohexene and (*Z*)-cyclooctene are less reactive than oct-1-ene, but cyclopentene is even more reactive than oct-1-ene.

Allyl chloride (entry 8) and 2-methylallyl chloride (entry 9) are both less reactive than oct-1-ene; this accords with the electrophilic character of the tosyl radical. The greater reactivity of the 2-methylallyl chloride may be the result of the

Table 1 Results of the light-promoted addition of TsI to alkenes, in CCl_4 or CH_2Cl_2, at room temperature

Alkene	Addition product	Yield (%)	M.p./°C	*t*/h
 **1**	 **1a**	89	Oil	2[a]
 **2**	 **2a**	77	95–97	0.25[b]
 **3**	 **3a**	73	93–95	1[a]
 **4**	 **4a**	74	74–76	0.25[b]
 **5**	 **5a**	78	Oil	0.25[b]
 **6**	 **6a**	78	45–46	0.25[b]
 **7**	 **7a**	87	Oil	0.25[b]
 **8**	 **8a**	86	Oil	2[a]
 **9**	 **9a**	80	104–107	3[a]
 **10**	 **10a**	91	77–79	1[c]
 **11**	 **11a**	86	76–77	2[c]

[a] Sunlight, CCl_4 [b] Philips lamp, HP/T-250 W, CH_2Cl_2 [c] Sunlight, CH_2Cl_2.

polar effect of the β-methyl group, which increases the electron density of the double bond thereby increasing the rate of attack by electrophilic radicals (such as tosyl) and decreasing the rate for nucleophilic ones (such as the cyclohexyl radical).[9]

It is worth noting that the delocalization of the unpaired electron of the radical adduct over the carbonyl group is not important, since methyl and butyl acrylates are less reactive than simple alkenes (oct-1-ene and hex-1-ene).

Allyl cyanide (entry 17) is the least reactive of all the alkenes because of the strong electron withdrawing power of the cyano group; the reactivity of vinyl cyanide (entry 18) is still very small, but a little bigger than that of allyl cyanide. Here, the polar deactivating effect of the CN group is still dominant, but the presence of some delocalization can be perceived, although it is very small.

For electrophilic radicals with low SOMO energy, the rate constant of addition decreases with increasing ionization potential (E_i) of the alkene (decreasing HOMO energy) and correlations between rates and E_i should be expected on the basis of simple frontier molecular orbital (FMO) considerations.[10] A rough linear relationship between E_i and $\log(k/k_0)$ for entries 2–6,12, 13, 16–18 (alkenes for which we could find E_i values in the literature)[11] was obtained.

$$\log(k/k_0) = 5.48 - 0.58\,(E_i/\mathrm{eV}); \quad r = 0.75$$

The greater reactivity of alkenes with methyl groups on the β-carbon shows the importance of the increase of the HOMO coefficient in the terminal carbon of the double bond,[12] which enhances the HOMO–SOMO interaction. This effect is also present in other alkene pairs (entries 10/11, 12/13 and 14/15).

Vinyl acetate (entry 16) is less reactive than oct-1-ene. A rough Hückel calculation shows that the acetoxy group in the vinyl acetate also increases (as with methyl, but to a much smaller extent) the HOMO coefficient on the β carbon atom of the double bond, but this is not sufficient to cancel the electron withdrawing power of the acetoxy group.

Table 4 shows the effect of the solvent on the relative rates of addition of cyclohexene, cyclopentene, (*Z*)-cyclooctene, vinylcyclohexane, allyl cyanide, and vinyl cyanide *vs.* oct-1-ene. For weakly polarized alkenes, such as cyclohexene, cyclopentene, and (*Z*)-cyclooctene, the effect of the solvent is small and erratic. However, for more strongly polarized alkenes, such as vinyl cyanide (entries 23, 29, 35) and allyl cyanide (entries 24, 30, 36) the change of the solvent leads to significant variations in the reactivity. In both cases the relative reactivities decrease as the solvent parameters[13] π^* (polarity/polarizability) and AN (acceptor number) increase.

Both empirical parameters of solvent polarity are a way of measuring the acceptor capacity of the solvent towards nonbonding electrons of nucleophiles. Being so, for alkenes in solution, it may be expected that the greater these parameters the greater the lowering of the HOMO energy of the alkenes by interaction with the LUMO of the solvent.

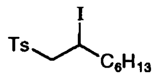
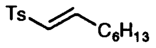
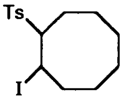
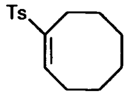
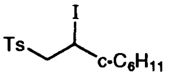
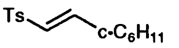
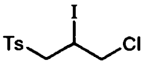
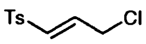
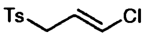
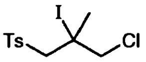
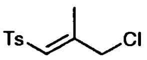
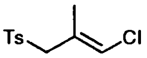
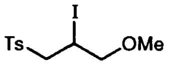
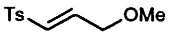
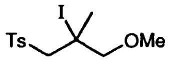
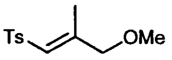
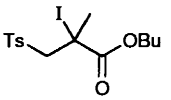
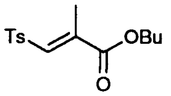
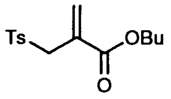
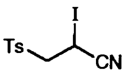
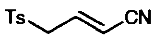
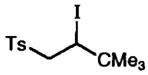
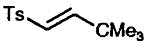
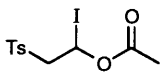
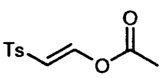
Table 4 shows that alkenes with greater E_i (lower HOMO energies), like vinyl cyanide and allyl cyanide, have relative reactivities much smaller than alkenes of smaller E_i (higher HOMO energies). This may be understood on the basis of FMO theory if we assume (Fig. 1) that the SOMO energy of tosyl radicals lies between the HOMO energies of oct-1-ene (M^1, 8–9 eV) and vinyl cyanide (M^2, 10.56 eV) or allyl cyanide (M^3, 10.95 eV). The HOMO energies of alkenes with greater E_i are less affected by solvent interaction than those with smaller E_i; SOMO energies of tosyl radicals are also less affected than the HOMO energies of alkenes on account of the different number of electrons in the HOMO and SOMO.

Under the circumstances, when we pass from a solvent of lower AN (or π^*), like carbon tetrachloride, to solvents of higher parameters (like dichloromethane or acetonitrile) the gap between the SOMO and HOMO energies is reduced (ΔE changes to $\Delta E'$) but ΔE_1 decreases more than ΔE_2 (or ΔE_3). The rate of addition to alkenes of smaller E_i (k_1) increases more than k_n ($n = 2, 3$). The result is that the relative rate k_n/k_1 decreases, as seen in Table 4.

Experimental

Materials.—Tosyl iodide was prepared from sodium 4-methylbenzenesulfinate.[14] Allyl methyl ether was prepared from prop-2-ynol[15] and methyl methylallyl ether from methylallyl chloride.[16] Oct-1-ene, hex-1-ene, cyclopentene,

Table 2 Unsaturated sulfones obtained from the addition products

Sulfone	Unsaturated sulfone	Yield (%)	M.p./°C	t/h
 **1a**	 **1b**	(E) 67 (Z) 10	Oil	1[a]
 **2a**	 **2b**	57	95–96	96[b]
 **3a**	 **3b**	79 93	Oil Oil	1[a] 3.5[b]
 **4a**	 **4b**  **4b′**	(E) 39 (Z) 15 (E) 8 (Z) 19	Wax	1[b]
 **5a**	 **5b**	(E) 30 (Z) 42	Oil	1[a]
	 **5b′**	(E) 30 (Z) 41	48–51	120[b]
 **6a**	 **6b**	(E) 62	72–74	1[a]
		(Z) 18	—	
 **7a**	 **7b**	(E) 47 (Z) 25	Oil	1[b]
 **8a**	 **8b**	(E) 39	Oil	2[a]
	 **8b′**	39		
 **9a**	 **9b**	(E) 45 (Z) 32	69–71	1.5[c]
 **10a**	 **10b**	58	50–52	30[b]
 **11a**	 **11b**	69	105–108	0.5[c]

[a] Boiling benzene. [b] Ethyl acetate, room temp. [c] Benzene, room temp.

Table 3 Relative reactivities of the reaction of tosyl radicals with alkenes $CH_2{=}CR{-}X$, in CH_3CN, at 25 °C

No.	R	X	Relative reactivity	Standard deviation	Number of runs	E_i/eV
	H	C_6H_{13}	(1)			
1	H	Bu	0.96	0.07 (7%)[b]	9	
2	H	Bu^t	0.58	0.06 (10%)	11	9.45[c]
3[a]	H	c-C_6H_{11}	0.83	0.04 (5%)	7	
4	H	Ph	14.8	4.53 (31%)	11	8.47[d]
5	Cyclohexene		0.75	0.03 (4%)	7	8.72[d]
6	Cyclopentene		2.31	0.25 (11%)	10	9.01[d]
7	(*Z*)-Cyclooctene		0.31	0.03 (10%)	10	
8	H	CH_2Cl	0.15	0.017 (11%)	8	
9	Me	CH_2Cl	0.84	0.05 (6%)	8	
10	H	CH_2OMe	0.29	0.008 (3%)	7	
11	Me	CH_2OMe	2.92	0.22 (8%)	7	
12	H	CO_2Me	0.35	0.009 (3%)	8	10.52[c]
13	Me	CO_2Me	1.49	0.21 (14%)	10	10.28[c]
14	H	CO_2Bu	0.52	0.05 (10%)	8	
15	Me	CO_2Bu	1.04	0.20 (19%)	10	
16	H	OCOMe	0.30	0.02 (6%)	7	9.77[c]
17	H	CH_2CN	0.067	0.009 (13%)	8	10.56[c]
18	H	CN	0.19	0.01 (5%)	7	10.95[c]

[a] Relative reactivities (k_n/k_1) indirectly calculated from results of competition experiments (Tables 3 and 5) as follows: $(k_n/k_0) = (k_n/k_m) \times (k_m/k_0)$. [b] Percent standard deviation. [c] Ref. 11(*a*). [d] Ref. 11(*b*).

Table 4 Relative reactivities (± standard deviations) of the reaction of tosyl radicals with alkenes $CH_2{=}CR{-}X$, in CCl_4, CH_2Cl_2 and CH_3CN, at 25 °C

R	X	CCl_4	No.	CH_3CN[c]	No.	CH_2Cl_2	No.
H	C_6H_{13}	(1)		(1)		(1)	
Cyclohexene		0.56 ± 0.02 (4%)[a]	19	0.75 ± 0.03 (4%)	25	0.66 ± 0.07 (11%)	31
Cyclopentene		1.98 ± 0.23 (12%)	20	2.31 ± 0.25 (11%)	26	2.35 ± 0.23 (10%)	32
(*Z*)-Cyclooctene		0.25 ± 0.03 (12%)	21	0.31 ± 0.03 (10%)	27	0.20 ± 0.03 (15%)	33[b]
H	c-C_6H_{11}	0.94 ± 0.04 (4%)	22	0.83 ± 0.04 (5%)	28	0.88 ± 0.11 (13%)	34[b]
H	CN	0.34 ± 0.06 (18%)	23[b]	0.19 ± 0.01 (5%)	29	0.056 ± 0.009 (16%)	35[b]
H	CH_2CN	0.11 ± 0.02 (18%)	24[b]	0.067 ± 0.009 (13%)	30	0.036 ± 0.008 (22%)	36[b]
	π^*[d]	0.28		0.75		0.82	
	AN[d]	8.6		18.9		20.4	

[a] Percent standard deviation. [b] Indirectly calculated from results of Tables 4 and 5 as follows: $(k_n/k_0) = (k_n/k_m) \times (k_m/k_0)$. [c] Results from Table 3. [d] Ref. 13.

Table 5 Relative reactivities of the reaction of tosyl radicals with alkenes, at 25 °C, used to calculate some relative reactivities presented in Tables 3 and 4

Alkenes	CCl_4	No.	CH_2Cl_2	No.	CH_3CN	No.
Vinyl cyanide/Cyclohexene	0.61 ± 0.11 (18%)	37	0.085 ± 0.013 (15%)	39		
Vinyl cyanide/Allyl cyanide	3.03 ± 0.22 (7%)	38	1.56 ± 0.26 (16%)	40		
Cyclohexene/(*Z*)-Cyclooctene			3.30 ± 0.30 (9%)	41		
Vinylcyclohexane/Cyclohexene			1.34 ± 0.10 (7%)	42	1.11 ± 0.03 (3%)	43

(*Z*)-cyclooctene, allyl chloride, methylallyl chloride, butyl methacrylate, allyl cyanide, vinyl acetate, 3,3-dimethylbut-1-ene and methyl methacrylate were commercial products (Aldrich), as were cyclohexene, vinyl cyanide and styrene (BDH). These chemicals and solvents (good grade commercial products) were used without further purification. IR and NMR spectra were recorded on a Philips PU 9800 or Mattson 5000 FTIR spectrometer and a Bruker AC-200 or AMX 300 spectrometer, respectively. When it seemed necessary, resonance multiplicities for ^{13}C were established *via* a DEPT sequence. The NMR chemical shifts are reported in the δ scale relative to Me_4Si as an internal standard; *J*-values are in Hz. Mass spectra were obtained on a Varian Saturn II GC 3400-MS instrument. Irradiation of solutions was carried out under visible light using either sunlight or a Philips HP/T 250 W lamp, for the specified time.

General Procedure for the Addition of Tosyl Iodide to Alkenes.—A solution of 2.0 g (7.1 mmol) of tosyl iodide (TsI) and an equivalent amount of alkene in dichloromethane or carbon tetrachloride (50–70 cm^3) was subjected to irradiation (Table 1). After irradiation, the coloured solution was successively washed with 10% aqueous sodium thiosulfate ($Na_2S_2O_3$) [or sodium metabisulfite ($Na_2S_2O_5$)], water, and dried ($CaCl_2$) and the solvent removed under reduced pressure to yield a residue which was purified and characterized.

General Procedure for the Dehydroiodination of the Adduct β-Iodo Sulfones.—To 2 mmol of the β-iodo sulfone, ethyl acetate or benzene (10 cm^3) was added, followed by 1.0 cm^3 of triethylamine, dropwise. In several cases the ammonium salt precpitated immediately, but in other cases the solution was left or refluxed for several hours (see Table 2), being always

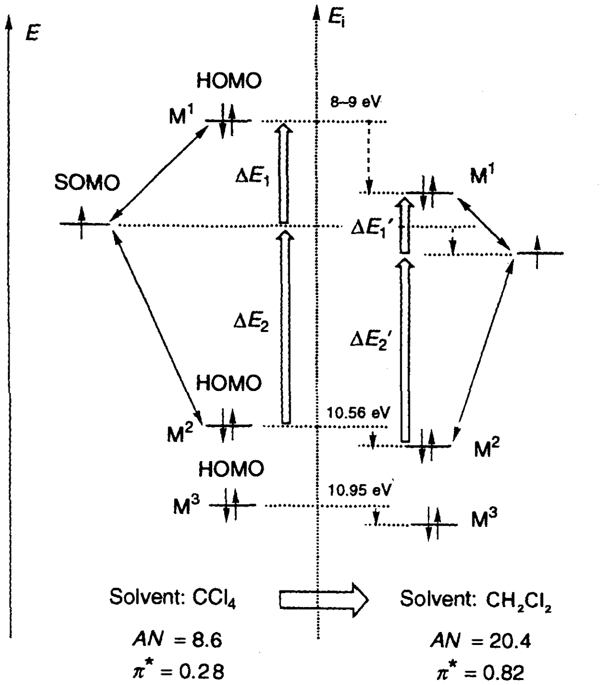


Fig. 1 FMO scheme showing the SOMO–HOMO interactions of tosyl radicals with monomers M_i in CCl_4 and CH_3CN (ΔE_3 and $\Delta E_3'$ are not depicted to avoid confusion)

monitored by TLC. The solution was diluted with 20–25 cm^3 of the solvent and filtered. The filtrate was successively washed with water and dilute aqueous HCl and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue treated as indicated in the corresponding unsaturated sulfones **1b**–**11b**.

2-*Iodo*-1-*tosyloctane* (**1a**).—Alkene **1** and TsI gave **1a** as a colourless liquid (89%); ν(liquid film)/cm^{-1} 3050, 2940, 2860, 1600, 1470, 1310, 1155, 1092, 825, 745, 680, 540 and 520; δ_H($CDCl_3$, 200 MHz) 7.77 (d, 2 H, *J* 8.2, Ar), 7.33 (d, 2 H, *J* 8.1, Ar), 4.43 (tdd, 1 H, *J* 9.2, 4.9, 3.7, CHI), 3.80 (dd, 1 H, *J* 14.2, 4.9, CH_2Ts), 3.70 (dd, 1 H, *J* 14.3, 9.2, CH_2Is), 2.46 (s, 3 H, CH_3Ar), 1.94–1.15 (m, 10 H, CH_2) and 0.89 (t, 3 H, *J* 6.5, CH_3CH_2); δ_C($CDCl_3$, 200 MHz) 144.46 (Ar), 135.90 (Ar), 129.52 (Ar), 127.41 (Ar), 64.99 (CH_2Ts), 38.40 (CH_2CHI), 30.94 (CH_2), 28.71 (CH_2), 27.51 (CH_2), 22.33 (CHI), 21.98 (CH_2CH_3), 21.10 (CH_3Ar) and 13.59 (CH_3CH_2); *m*/*z* 267 (M – I, 13%), 139 (100), 111 (6), 91 (4) and 41 (4).

(E)- *and* (Z)-1-*Tosyloct*-1-*ene* (**1b**).—Octane **1a** gave octene **1b** as a colourless liquid (77%); ν(liquid film)/cm^{-1} 3047, 2929, 2858, 1626, 1597, 1459, 1303, 1145, 1088, 965, 814, 661, 577 and 540; δ_H($CDCl_3$, 200 MHz) 7.80 (d, 2 H, *J* 8.4, Ar, *Z*), 7.76 (d, 2 H, *J* 8.3, Ar, *E*), 7.32 (d, 2 H, *J* 8.3, Ar, *E* and *Z*), 6.96 (dt, 1 H, *J* 15.1, 6.8, =CH–C, *E*), 6.30 (dt, 1 H, *J* 15.1, 1.5, =CH–Ts, *E*), 6.33–6.10 (m, 2 H, CH=CH, *Z*), 2.64 (dt, 2 H, *J* 7.0, 6.8, CH_2–C=, *Z*), 2.42 (s, 3 H, CH_3Ar, *E* and *Z*), 2.22 (tdd, 2 H, *J* 7.3, 6.8, 1.5, CH_2–C=, *E*), 1.5–1.2 (complex, 8 H, CH_2, *E* and *Z*) and 0.86 (2 t, 3 H, CH_3CH_2, *E* and *Z*); δ_C($CDCl_3$, 200 MHz) 146.99 (=$CHCH_2$, *Z*), 146.56 (=$CHCH_2$, *E*), 144.02 (Ar), 137.67 (Ar), 130.45 (=CHTs), 129.70 (Ar), 127.42 (Ar), 31.29 (CH_2), 28.51 (CH_2), 27.40 (CH_2), 22.31 (CH_2CH_3), 21.43 (CH_3Ar), and 13.85 (CH_3CH_2); (*Z*) *m*/*z* 266 (M$^+$, 24%), 209 (59), 196 (22), 157 (100), 139 (55), 117 (22), 110 (26), 92 (33), 91 (62), 81 (30), 69 (22), 68 (23), 67 (24), 65 (38), 55 (21), 54 (20), 53 (25), 43 (22), 41 (51), 39 (33), 29 (30) and 27 (24); (*E*) *m*/*z* 266 (M$^+$, 4%), 209 (14), 183 (32), 157 (95), 139 (100), 117 (11), 111 (37), 110 (75), 92 (41), 91 (62), 81 (47), 69 (53), 68 (36), 67 (40), 65 (52), 55 (37), 54 (19), 53 (17), 43 (45), 41 (83), 39 (46), 29 (48) and 27 (37).

trans-1-*Iodo*-2-*tosylcyclooctane* (**2a**).—Octene **2** and TsI gave **2a** as a solid (77%), m.p. 95–97 °C (ethanol) (Found: C, 45.6; H, 5.4; S, 8.2. $C_{15}H_{21}IO_2S$ requires C, 45.93; H, 5.40; S, 8.17%); ν(KBr disk)/cm^{-1} 3043, 2921, 2879, 1600, 1464, 1448, 1303, 1141, 1086, 810, 734, 665 and 528; δ_H($CDCl_3$, 200 MHz) 7.82 (d, 2 H, *J* 8.0, Ar), 7.27 (d, 2 H, *J* 8.0, Ar), 4.88 (ddd, 1 H, *J* 6.6, 6.5, 1.9, CHI), 3.56 (ddd, 1 H, *J* 8.3, 6.6, 1.4, CHTs), 2.47 (s, 3 H, CH_3Ar) and 2.00–1.50 (m, 12 H, CH_2); δ_C($CDCl_3$, 300 MHz) 145.01 (Ar), 134.92 (Ar), 129.92 (Ar), 129.17 (Ar), 73.73 (CHTs), 33.12 (CH_2), 29.06 (CH_2), 27.88 (CH_2), 26.85 (CH_2), 25.81 (CHI), 24.71 (CH_2), 23.87 (CH_2) and 21.70 (CH_3Ar).

1-*Tosylcyclooctene* **2b**.—Octane **2a** gave octene **2b** as a solid (57%), m.p. 95–96 °C (ethanol); ν(Nujol)/cm^{-1} 1644, 1595, 1463, 1455, 1377, 1298, 1147, 1121, 1084, 820, 714, 697 and 568; δ_H($CDCl_3$, 300 MHz) 7.75 (d, 2 H, *J* 8.2, Ar), 7.31 (d, 2 H, *J* 8.2, Ar), 7.07 (t, 1 H, *J* 8.6, CH=), 2.43 (s, 3 H, CH_3Ar) and 2.38–1.25 (complex, 12 H, CH_2); δ_C($CDCl_3$, 300 MHz) 143.91 (Ar), 141.98 (C=), 140.63 (C=), 136.90 (Ar), 129.66 (Ar), 128.17 (Ar), 29.08 (CH_2), 28.21 (CH_2), 26.42 (CH_2), 25.79 (CH_2), 25.57 (CH_2), 25.02 (CH_2) and 21.56 (CH_3Ar); *m*/*z* 264 (M$^+$, 35%), 157 (32), 139 (24), 109 (45), 108 (43), 93 (24), 92 (16), 91 (29), 81 (21), 80 (28), 79 (35), 67 (100), 65 (31), 55 (40), 53 (21), 41 (45), 38 (27) and 27 (15).

1-*Cyclohexyl*-1-*iodo*-2-*tosylethane* (**3a**).—Alkene **3** and TsI gave ethane **3a** as a solid (73%), m.p. 93–95 °C (methanol) (Found: C, 45.6; H 5.4; S, 8.1; O, 8.2. $C_{15}H_{21}IO_2S$ requires C, 45.93; H, 5.40; S, 8.17; O, 8.16%); ν(Nujol)/cm^{-1} 1600, 1300, 1150, 830, 745, 685 and 530; δ_H($CDCl_3$, 200 MHz) 7.79 (d, 2 H, *J* 8.3, Ar), 7.38 (d, 2 H, *J* 8.1, Ar), 4.49 (ddd, 1 H, *J* 8.7, 5.5, 2.1, CHI), 3.81 (dd, 1 H, *J* 14.6, 8.7, CH_2Ts), 3.70 (dd, 1 H, *J* 14.6, 5.5, CH_2Ts), 2.47 (s, 3 H, CH_3Ar) and 1.8–0.9 (complex, 11 H, cyclohexyl); δ_C($CDCl_3$, 200 MHz) 145.20 (Ar), 136.45 (Ar), 130.06 (Ar), 128.05 (Ar), 63.41 (CH_2Ts), 42.19 (CH in cyclohexyl), 34.22 (CH_2), 32.75 (CHI), 29.32 (CH_2), 25.96 (CH_2), 25.57 (CH_2), 25.28 (CH_2) and 21.67 (CH_3Ar); *m*/*z* 265 (M – I, 6%), 157 (49), 139 (26), 109 (100), 91 (30), 81 (21), 67 (64) and 41 (28).

(E)-1-*Cyclohexyl*-2-*tosylethene* (**3b**).—Ethane **3a** gave ethene **3b** as a colourless liquid (93%); ν(liquid film)/cm^{-1} 3060, 2940, 2860, 1630, 1605, 1455, 1310, 1145, 1090, 980, 840, 820, 670 and 550; δ_H($CDCl_3$, 200 MHz) 7.75 (d, 2 H, *J* 8.3, Ar), 7.32 (d, 2 H, *J* 8.3, Ar), 6.92 (dd, 1 H, *J* 15.2, 6.4, CH=C–Ts), 6.23 (dd, 1 H, *J* 15.2, 1.5, =CH–Ts), 2.43 (s, 3 H, CH_3Ar), 2.19–2.15 (m, 1 H, CH, cyclohexyl), 1.8–1.6 (complex, 5 H, cyclohexyl) and 1.4–1.0 (complex, 5 H, cyclohexyl); δ_C($CDCl_3$, 200 MHz) 151.09 (CH=), 144.03 (Ar), 137.8 (Ar), 129.77 (Ar), 128.52 (=CH–Ts), 127.50 (Ar), 39.75 (CH in cyclohexyl), 31.21 (CH_2), 25.66 (CH_2), 25.48 (CH_2) and 21.51 (CH_3Ar).

1-*Chloro*-2-*iodo*-3-*tosylpropane* (**4a**).—Alkene **4** and TsI gave propane **4a** as a solid (74%) m.p. 74–76 °C (methanol) (Found: C, 33.6; H, 3.5; S, 8.75. $C_{10}H_{12}ClIO_2S$ requires: C, 33.49; H, 3.37; S, 8.94%); ν(Nujol)/cm^{-1} 1600, 1300, 1145, 1095, 920, 860, 820, 810, 700, 540 and 520; δ_H($CDCl_3$, 200 MHz) 7.81 (d, 1 H, *J* 8.3, Ar), 7.40 (d, 2 H, *J* 8.5, Ar), 4.69–4.61 (m, 1 H, CHI), 4.11 (dd, 1 H, *J* 12.1, 4.6, CH_2Ts), 3.97 (dd, 1 H, 14.6, 8.0, CH_2Cl), 3.90 (dd, 1 H, *J* 12.1, 5.9, CH_2Ts), 3.61 (dd, 1 H, *J* 14.6, 5.5, CH_2Cl) and 2.47 (s, 3 H, CH_3Ar); δ_C($CDCl_3$, 200 MHz) 145.54 (Ar), 135.87 (Ar), 130.20 (Ar), 128.11 (Ar), 61.95 (CH_2Ts), 50.07 (CH_2Cl), 21.70 (CH_3Ar) and 16.26 (CHI); *m*/*z* 359 (M$^+$, 1%), 323 (5), 233 (13), 231 (38), 203 (11), 195 (12), 167 (4), 155 (89), 139 (75), 131 (16), 107 (8), 91 (100), 77 (16), 75 (22), 65 (58) and 51 (10).

3-*Chloro*-1-*tosylprop*-1-*ene* (**4b**) *and* 1-*Chloro*-3-*tosylprop*-1-*ene* (**4b′**).—Sulfone **4a** gave a wax (81%) formed by a mixture of (*E*) and (*Z*) isomers of **4b** and **4b′**: 39, 15, 8 and 19%, respectively. When the reaction time was much longer (24 h), the isomer **4b** was completely transformed into **4b′** as a solid (74%, *E*/*Z* = 26:74), m.p. 49–53 °C (methanol). Equimolar amounts of Et_3N and sulfone **4a** and reaction time of only 5 min gave isomer **4b** as a wax (54%, *E*:*Z* = 79:21).

4b, *E*:*Z* = 79:21: ν(liquid film)/cm^{-1} 3060, 2940, 1640, 1600, 1500, 1450, 1400, 1300, 1150, 1090, 980, 820, 715, 665, 595, 580 and 540; δ_H($CDCl_3$, 200 MHz) 7.80 (2 d, 2 H, *J* 8, Ar, *E* and *Z*), 7.39–7.33 (m, 2 H, Ar, *E* and *Z*), 7.01 (dt, 1 H, *J* 14.8, 5.1, $=C\mathit{H}CH_2Cl$, *E*), 6.66 (dt, 1 H, *J* 14.8, 1.7, =CHTs, *E*); 6.34–6.29 (m, 2 H, CH=CH, *Z*), 4.76–4.73 (m, 2 H, CH_2Cl, *Z*), 4.20 (dd, 2 H, 5.1, 1.7, CH_2Cl, *E*) and 2.45 (s, 3 H, CH_3Ar, *E* and *Z*); δ_C($CDCl_3$, 300 MHz) 145.16 (Ar, *Z*), 144.89 (Ar, *E*), 139.30 (=CHTs, *Z*), 139.23 (=CHTs, *E*), 136.64 (Ar, *E*), 136.47 (Ar, *Z*), 133.70 ($=\mathit{C}HCH_2Cl$, *E*), 132.08 ($=\mathit{C}HCH_2Cl$, *Z*), 130.41 (Ar, *Z*), 130.15 (Ar, *E*), 127.88 (Ar, *E*), 127.55 (Ar, *Z*), 41.37 (CH_2Cl, *E*), 37.25 (CH_2Cl, *Z*), 21.65 (CH_3Ar); *Z*: *m*/*z* 231 (M^+, 10%), 230 (23), 213 (16), 195 (28), 177 (24), 155 (14), 139 (24), 129 (20), 91 (100), 77 (31), 75 (21), 65 (76) and 51 (18); *E*: *m*/*z* 231 (M^+, 7%), 215 (1), 195 (2), 155 (12), 139 (100), 131 (24), 107 (16), 91 (63), 77 (19), 75 (11), 65 (49) and 51 (12).

4b′, *E*:*Z* = 24:72: ν(liquid film)/cm^{-1} 3100, 3000, 2940, 1635, 1600, 1450, 1405, 1310, 1160, 1095, 945, 905, 825, 760, 720, 580 and 520; δ_H($CDCl_3$, 200 MHz) 7.75 (2 d, 2 H, *J* 8, Ar, *E* and *Z*), 7.42–7.38 (m, 2 H, Ar, *E* and *Z*), 6.30 (dt 1 H, *J* 7.3, 1.2, =CHCl, *Z*), 6.10 (dt, 1 H, *J* 13.5, 1.0, =CHCl, *E*), 5.89 (dt, 1 H, *J* 7.6, 7.3, $=CHCH_2Ts$, *Z*), 5.87 (dt, 1 H, *J* 13.5, 7.8, $=CHCH_2Ts$, *E*), 4.04 (dd, 2 H, *J* 7.6, 1.2, CH_2Ts, *Z*), 3.78 (dd, 2 H, *J* 7.8, 1.0, CH_2Ts, *E*) and 2.44 (s, 3 H, CH_3Ar, *E* and *Z*); δ_C($CDCl_3$, 200 MHz) 144.88 (Ar), 135.27 (Ar), 129.77 ($=\mathit{C}HCH_2$, *Z*), 129.66 (Ar), 128.25 (Ar), 127.42 ($=\mathit{C}HCH_2$, *E*), 120.17 (=CHCl, *E*), 116.62 (=CHCl, *Z*), 57.82 (CH_2Ts, *E*), 54.67 (CH_2Ts, *Z*) and 21.52 (CH_3Ar, *E* and *Z*); *Z*: *m*/*z* 231 (M^+, 1%), 195 (8), 155 (58), 139 (9), 131 (13), 91 (100), 77 (27), 75 (50) and 65 (44); *E*: *m*/*z* 195 (M − ClH, 8%), 155 (56), 139 (10), 131 (13), 91 (100), 77 (20), 75 (83) and 65 (49).

1-*Chloro*-2-*iodo*-2-*methyl*-3-*tosylpropane* (**5a**).—Alkene **5** and TsI gave propane **5a** as a solid (78%), m.p. 41–44 °C (methanol) (Found: C, 35.15; H, 3.7; S, 8.8. $C_{11}H_{14}ClIO_2S$ requires: C, 35.45; H, 3.79; S, 8.60%); ν(Nujol)/cm^{-1} 1600, 1310, 1280, 1255, 1225, 1165, 1150, 1090, 1050, 825, 755, 730, 680 and 520; δ_H($CDCl_3$, 200 MHz) 7.82 (d, 2 H, *J* 8.3, Ar), 7.39 (d, 2 H, *J* 8.1, Ar), 4.17 (d, 1 H, *J* 12.1, CH_2Ts), 4.10 (d, 1 H, *J* 12.1, CH_2Ts), 4.02 (d, 1 H, *J* 14.3, CH_2Cl), 3.82 (d, 1 H, *J* 14.3, CH_2Cl), 2.46 (s, 3 H, CH_3Ar) and 2.38 (s, 3 H, CH_3CI); δ_C($CDCl_3$, 200 MHz) 145.26 (Ar), 137.48 (Ar), 130.08 (Ar), 127.84 (Ar), 66.87 (CH_2Ts), 56.51 (CH_2Cl), 39.67 (CI), 32.93 ($\mathit{C}H_3CI$) and 21.66 (CH_3Ar).

3-*Chloro*-2-*methyl*-1-*tosylprop*-1-*ene* (**5b**) *and* 1-*Chloro*-2-*methyl*-3-*tosylprop*-1-*ene* (**5b′**).—Sulfone **5a′** gave propene **5b** as a pale yellow oil (72%, *E*:*Z* = 42:58). When the reaction time was much longer (120 h), the isomer **5b** was completely transformed into **5b′** as a solid (71%, *E*:*Z* = 42:58), m.p. 48–51 °C (methanol).

5b, *E*:*Z* = 42:58: ν(liquid film)/cm^{-1} 3050, 2920, 1630, 1600, 1440, 1305, 1145, 1090, 870, 820, 710, 665 and 590; δ_H($CDCl_3$, 200 MHz) 7.83–7.78 (m, 2 H, Ar, *Z* and *E*), 7.36 (2 d, *J* 8, Ar, *Z* and *E*), 6.49 (m, 1 H, *J* 1.2, =CHTs, *E*), 6.22–6.21 (m, 1 H, =CHTs, *Z*), 4.69 (d, 2 H, *J* 0.4, CH_2Cl, *Z*), 4.00 (d, 2 H, *J* 1.2, CH_2Cl, *E*), 2.44 (s, 3 H, CH_3Ar, *Z* and *E*), 2.23 (d, 3 H, *J* 1.3, $CH_3C=$, *E*) and 2.01 (d, 3 H, *J* 1.4, $CH_3C=$, *Z*); δ_C($CDCl_3$, 300 MHz) 149.26 ($=\mathit{C}CH_2Cl$), 148.81 ($=\mathit{C}CH_2Cl$), 144.69 (Ar), 144.55 (Ar), 138.37 (Ar), 137.95 (Ar), 129.98 (Ar), 129.92 (Ar), 129.31 (=CHTs), 129.19 (=CHTs), 127.43 (Ar), 127.33 (Ar), 48.53 (CH_2Cl, *E*), 40.01 (CH_2Cl, *Z*), 22.87 ($\mathit{C}H_3C$), 21.61 (CH_3Ar) and 15.81 ($\mathit{C}H_3C=$); *Z*: *m*/*z* 247 (M^+ + 2, 23%), 245 (M^+, 71), 211 (20), 209 (48), 191 (43), 178 (58), 143 (100), 139 (56), 128 (25), 111 (10), 91 (67), 65 (62) and 53 (66); *E*: *m*/*z* 247 (M^+ + 2, 17%), 245 (M^+, 49%), 211 (22), 177 (12), 143 (100), 128 (15), 111 (12), 91 (46), 65 (49) and 53 (39).

5b′, *E*:*Z* = 42:58: (Found: C, 53.55; H, 5.3; S, 13.2. $C_{11}H_{13}ClO_2S$ requires C, 53.99; H, 5.36; S, 13.1%); ν(liquid film)/cm^{-1} 3060, 2940, 1635, 1605, 1445, 1310, 1150, 1095, 875, 825, 715, 670 and 595; δ_H($CDCl_3$, 200 MHz) 7.79–7.71 (2 d, 2 H, *J* 8, Ar, *Z* and *E*), 7.38–7.31 (2 d, 2 H, *J* 8, Ar, *Z* and *E*), 6.00–5.98 (m, 1 H, =CHCl, *E*), 5.79–5.77 (m, 1 H, =CHCl, *Z*), 4.03 (s, 2 H, CH_2Ts, *E*), 3.77 (d, 2 H, *J* 0.8, CH_2Ts, *Z*), 2.46 (s, 3 H, CH_3Ar), 2.45 (s, 3 H, CH_3Ar), 2.00 (d, 3 H, *J* 1.6, $CH_3C=$, *E*) and 1.89 (d, 3 H, *J* 1.5, $CH_3C=$, *Z*); δ_C($CDCl_3$, 300 MHz) 144.09 (Ar), 143.93 (Ar), 134.60 (Ar), 133.99 (Ar), 128.83 (Ar), 128.69 (Ar), 127.48 (Ar), 127.43 (Ar), 126.35 ($=\mathit{C}CH_3$), 126.31 ($=\mathit{C}CH_3$), 120.98 (=CHCl), 118.92 (=CHCl), 62.28 (CH_2Ts), 57.95 (CH_2Ts), 20.67 (CH_3Ar), 20.20 ($\mathit{C}H_3C=$) and 16.35 ($\mathit{C}H_3C=$); *Z*: *m*/*z* 209 (M − ClH, 27%) 155 (6), 139 (13), 89 (100), 65 (36) and 53 (93); *E*: *m*/*z* 209 (M − ClH; 32%), 155 (13), 139 (13), 91 (80), 89 (92), 65 (42) and 53 (100).

2-*Iodo*-1-*methoxy*-3-*tosylpropane* (**6a**).—Alkene **6** and TsI gave propane **6a** as a solid (78%), m.p. 45–46 °C (methanol) (Found: C, 37.35; H, 4.3; S, 9.1. $C_{11}H_{15}IO_3S$ requires: C, 37.30; H, 4.27; S, 9.05%); ν(Nujol)/cm^{-1} 1602, 1305, 1275, 1140, 1080, 1025, 815, 750, 690 and 520; δ_H($CDCl_3$, 200 MHz) 7.80 (d, 2 H, *J* 8.4, Ar), 7.38 (d, 2 H, *J* 8.4, Ar), 4.54–4.47 (m, 1 H, CHI), 3.91 (dd, 1 H, *J* 14.5, 8.6, CH_2Ts), 3.67 (dd, 1 H, *J* 13.0, 1.9, CH_2O), 3.65 (dd, 1 H, *J* 13.1, 2.0, CH_2O), 3.59 (dd, 1 H, *J* 14.5, 5.2, CH_2Ts), 3.37 (s, 3 H, CH_3O) and 2.46 (s, 3 H, CH_3Ar); δ_C($CDCl_3$, 200 MHz) 145.19 (Ar), 136.15 (Ar), 130.03 (Ar), 128.00 (Ar), 75.78 (CH_2O), 61.76 (CH_2Ts), 58.63 (CH_3O), 21.62 (CH_3Ar) and 16.21 (CHI).

3-*Methoxy*-1-*tosylprop*-1-*ene* (**6b**).—Sulfone **6a** gave propene **6b** as a solid (80%, *E*:*Z* = 77:23), m.p. 62–67 °C. Recrystallization from methanol gave (*E*)-**6b**, as a pale yellow solid, m.p. 72–74 °C.

6b, *E*:*Z* = 77:23): ν(Nujol)/cm^{-1} 3030, 1635, 1600, 1305, 1190, 1150, 1120, 1090, 1035, 970, 820, 710, 690, 620 and 530; δ_H($CDCl_3$, 300 MHz) 7.80–7.74 (m, 2 H, *E* and *Z*), 7.37–7.28 (m, 2 H, *E* and *Z*), 6.94 (dt, 1 H, *J* 15.1, 3.5, $=C\mathit{H}CH_2$, *E*), 6.59 (dt, 1 H, *J* 15.0, 2.2, =CHTs, *E*), 6.35 (dt, 1 H, *J* 11.5, 4.7, $=C\mathit{H}CH_2$, *Z*), 6.26 (dt, 1 H, *J* 11.5, 1.9, =CHTs, *Z*), 4.61 (dd, 2 H, *J* 4.7, 1.9, CH_2O, *Z*), 4.11 (dd, 2 H, *J* 3.4, 2.1, CH_2O, *E*), 3.37 (s, 3 H, CH_3O, *Z*), 3.36 (s, 3 H, CH_3O, *E*), 2.45 (s, 3 H, CH_3Ar, *Z*) and 2.43 (s, 3 H, CH_3Ar, *E*); δ_C($CDCl_3$, 300 MHz) 144.80 (Ar, *Z*), 144.40 (Ar, *E*), 143.77 ($=\mathit{C}HCH_2$, *Z*), 141.73 ($=\mathit{C}HCH_2$, *E*), 137.82 (Ar *Z*), 137.31 (Ar, *E*), 130.61 (=CHTs, *Z* and *E*), 130.00 (Ar, *Z*), 129.90 (Ar, *E*), 127.73 (Ar, *E*), 127.37 (Ar, *Z*), 70.04 (CH_2O, *E*), 68.25 (CH_2O, *Z*), 58.88 (CH_3O, *E*), 58.63 (CH_3O, *Z*), 21.64 (CH_3Ar, *Z*) and 21.60 (CH_3Ar, *E*); *Z*: *m*/*z* 226 (M^+, 4%), 195 (8), 139 (15), 91 (19), 71 (100), 65 (18), 45 (11) and 41 (38); *E*: *m*/*z* 226 (M^+, 1%), 195 (1), 139 (12), 91 (9), 71 (100), 65 (9), 45 (11) and 41 (13).

E, **6b**: (Found: C, 58.1; H, 6.2. $C_{11}H_{14}O_3S$ requires: C, 58.38; H, 6.23%); ν(Nujol)/cm^{-1} 3030, 1635, 1600, 1305, 1190, 1150, 1125, 1090, 1035, 970, 840, 820, 785, 715, 680 and 620; δ_H($CDCl_3$, 200 MHz) 7.77 (d, 2 H, *J* 8.2, Ar), 7.32 (d, 2 H, *J* 8.2, Ar), 6.94 (dt, 1 H, *J* 15.1, 3.5, $=C\mathit{H}CH_2$), 6.59 (dt, 1 H, *J* 15.1, 2.1, =CHTs), 4.11 (dd, 2 H, *J* 3.4, 2.1, CH_2O), 3.36 (s, 3 H, CH_3O) and 2.43 (s, 3 H, CH_3Ar); δ_C($CDCl_3$, 200 MHz) 144.34

(Ar), 141.63 (=*C*HCH$_2$), 137.35 (Ar), 130.68 (=CHTs), 129.66 (Ar), 127.72 (Ar), 70.03 (CH$_2$O), 58.85 (CH$_3$O) and 21.56 (CH$_3$Ar).

2-*Iodo*-2-*methyl*-1-*methoxy*-3-*tosylpropane* (**7a**).—Alkene **7** and TsI gave propane **7a** as a pale yellow oil (87%); ν(liquid film)/cm^{-1} 3000, 2940, 2840, 1600, 1450, 1400, 1320, 1150, 1090, 820, 740, 680 and 520; δ_H(CDCl$_3$, 200 MHz) 7.78 (d, 2 H, *J* 8.3, Ar), 7.36 (d, 2 H, *J* 8.4, Ar), 4.12 (d, 1 H, *J* 14.0, CH$_2$Ts), 3.77 (d, 1 H, *J* 14.0, CH$_2$Ts), 3.64 (s, 2 H, CH$_2$O), 3.43 (s, 3 H, CH$_3$O), 2.44 (s, 3 H, CH$_3$Ar) and 2.30 (s, 3 H, CH$_3$CI); δ_C(CDCl$_3$, 200 MHz) 144.84 (Ar), 137.74 (Ar), 129.86 (Ar), 127.69 (Ar), 81.06 (CH$_2$O), 67.17 (CH$_2$Ts), 58.69 (CH$_3$O), 41.77 (CI), 31.06 (*C*H$_3$CI) and 21.55 (CH$_3$Ar).

(E)- *and* (Z)-3-*Methoxy*-2-*methyl*-1-*tosylprop*-1-*ene* (**7b**).—Sulfone **7a** gave propene **7b** as a pale yellow oil (72%, *E*:*Z* = 65:35); ν(liquid film)/cm^{-1} 3030, 2925, 2825, 1640, 1600, 1450, 1380, 1305, 1145, 1090, 820, 780, 710 and 665; δ_H(CDCl$_3$, 300 MHz) 7.80–7.77 (m, 2 H, Ar, *E* and *Z*), 7.36–7.31 (m, 2 H, Ar, *E* and *Z*), 6.45 (m, 1 H, *J* 1.4, =CHTs, *E*), 6.23 (m, 1 H, *J* 1.4, =CHTs, *Z*), 4.51 (d, 2 H, *J* 0.7, CH$_2$O, *Z*), 3.85 (d, 2 H, *J* 1.4, CH$_2$O, *E*), 3.32 (s, 3 H, CH$_3$O, *E*), 3.30 (s, 3 H, CH$_3$O, *Z*), 2.44 (s, 3 H, CH$_3$Ar, *Z*), 2.43 (s, 3 H, CH$_3$Ar, *E*), 2.07 (d, 3 H, *J* 1.1 CH$_3$C=, *E*) and 1.93 (d, 3 H, *J* 1.3, CH$_3$C=, *Z*); δ_C(CDCl$_3$, 300 MHz) 153.52 (=*C*CH$_3$, *Z*), 151.86 (=*C*CH$_3$, *E*), 144.33 (Ar, *Z*), 144.07 (Ar, *E*), 139.19 (Ar, *E*), 138.84 (Ar, *Z*), 129.89 (Ar, *Z*), 129.79 (Ar, *E*), 127.63 (Ar, *Z*), 127.20 (Ar, *E*), 125.24 (=CHTs, *E* and *Z*), 75.46 (CH$_2$O, *E*), 69.21 (CH$_2$O, *Z*), 58.67 (CH$_3$O, *E*), 58.46 (CH$_3$O, *Z*), 21.59 (CH$_3$Ar, *E*), 21.58 (CH$_3$Ar, *Z*), 14.47 (*C*H$_3$C=, *E* and *Z*); *E*: *m*/*z* 240 (M$^+$, 6%), 139 (16), 91 (20), 85 (100), 69 (10), 65 (19), 55 (26), 45 (51) and 39 (20); *Z*: *m*/*z* 240 (M$^+$, 40%), 225 (15), 139 (40), 129 (15), 92 (26), 91 (46), 85 (100), 69 (97), 65 (49), 55 (50), 45 (71), 41 (53) and 39 (62).

Butyl 2-*Iodo*-2-*methyl*-3-*tosylpropanoate* (**8a**).—Alkene **8** and TsI gave ester **8a** as a pale yellow oil (86%), ν(liquid film)/cm^{-1} 2970, 2940, 2890, 1735, 1600, 1459, 1408, 1390, 1325, 1295, 1175, 1150, 1090, 835, 743, 660 and 520; δ_H(CDCl$_3$, 300 MHz) 7.77 (d, 2 H, *J* 8.3, Ar), 7.37 (d, 2 H, *J* 8.2, Ar), 4.48 (d, 1 H, *J* 13.8, CH$_2$Ts), 4.25 and 4.15 (m, 2 H, *J* 10.8, 6.6, CH$_2$O), 3.93 (d, 1 H, *J* 13.8, CH$_2$Ts), 2.45 and 2.43 (2 s, 6 H, CH$_3$Ar and CH$_3$CI), 1.7–1.6 (m, 2 H, C*H*$_2$Et), 1.5–1.4 (m, 2 H, C*H*$_2$Me) and 0.97 (t, 3 H, *J* 7.3, C*H*$_3$CH$_2$); δ_C(CDCl$_3$, 200 MHz) 170.83 (C=O), 144.96 (Ar), 137.41 (Ar), 129.83 (Ar), 127.60 (Ar), 68.53 (CH$_2$Ts), 66.16 (CH$_2$O), 29.94 and 29.79 (*C*H$_2$Et and *C*I), 29.57 (*C*H$_3$CI), 21.46 (CH$_3$Ar), 18.89 (*C*H$_2$Me) and 13.53 (*C*H$_3$CH$_2$).

Butyl 2-*Methyl*-3-*tosylprop*-2-*enoate* (**8b**) *and Butyl* 2-*Tosylmethylprop*-2-*enoate* (**8b′**).—Sulfone **8a** gave a colourless oil (78%); the ^{1}H NMR spectrum of which showed that it was a 1:1 mixture of **8b** and **8b′**. The mixture was column chromatographed on silica gel (Merck, art. 7754) to give pure **8b** and **8b′**.

8b: ν(liquid film)/cm^{-1} 3060, 2980, 2940, 2890, 1720, 1630, 1600, 1465, 1390, 1325, 1305, 1240, 1155, 1090, 820, 785, 740, 710 and 575; δ_H(CDCl$_3$, 200 MHz) 7.83 (d, 2 H, *J* 8.3, Ar), 7.38 (d, 2 H, *J* 8.0, Ar), 7.23 (q, 1 H, *J* 1.5, =CH), 4.17 (t, 2 H, *J* 6.6, CH$_2$O), 2.45 (s, 3 H, CH$_3$Ar), 2.32 (d, 3 H, *J* 1.5, CH$_3$C=), 1.3–1.4 (m, 2 H, C*H*$_2$Et), 1.7–1.6 (m, 2 H, C*H*$_2$Me) and 0.93 (t, 3 H, *J* 7.2, C*H*$_3$CH$_2$); δ_C(CDCl$_3$, 200 MHz) 165.55 (C=O), 145.01 (Ar), 141.06 (=CMe), 137.28 (Ar), 137.28 (=CH), 129.95 (Ar), 127.56 (Ar), 65.95 (CH$_2$O), 30.26 (*C*H$_2$Et), 21.51 (CH$_3$Ar), 18.93 (*C*H$_2$Me), 13.49 (*C*H$_3$CH$_2$) and 13.19 (*C*H$_3$C=); *m*/*z* 296 (M$^+$, 14%), 241 (17), 223 (20), 222 (100), 207 (20), 158 (10), 155 (27), 139 (94), 130 (27), 119 (24), 91 (68), 65 (33), 41 (33) and 29 (35).

8b′: ν(liquid film)/cm^{-1} 3065, 2980, 2940, 2890, 1725, 1635, 1605, 1465, 1415, 1320, 1250, 1190, 1150, 1090, 968, 900, 820, 715, 675, 560 and 520; δ_H(CDCl$_3$, 200 MHz) 7.73 (d, 2 H, *J* 8.2, Ar), 7.32 (d, 2 H, *J* 8.0, Ar), 6.49 (d, 1 H, *J* 0.6, =CH$_2$), 5.90 (d, 1 H, *J* 0.6, =CH$_2$), 4.14 (s, 2 H, CH$_2$Ts), 3.97 (t, 2 H, *J* 6.5, CH$_2$O), 2.44 (s, 3 H, CH$_3$Ar), 1.5–1.4 (m, 2 H, C*H*$_2$Et), 1.4–1.3 (m, 2 H, C*H*$_2$Me) and 0.92 (t, 3 H, *J* 7.2, C*H*$_3$CH$_2$); δ_C(CDCl$_3$, 200 MHz) 164.76 (C=O), 144.74 (Ar), 135.27 (Ar), 133.06 (C=C), 129.53 (Ar), 129.09 (C=C), 128.65 (Ar), 65.18 (CH$_2$O), 57.39 (CH$_2$Ts), 30.28 (CH$_2$Et), 21.53 (CH$_3$Ar), 18.94 (*C*H$_2$Me) and 13.58 (*C*H$_3$CH$_2$); *m*/*z* 232 (M − SO$_2$, 22%), 223 (13), 176 (22), 155 (63), 139 (18), 130 (16), 91 (100), 85 (23), 68 (35), 65 (26), 41 (26), 40 (22) and 29 (24).

3-*Iodo*-4-*tosylbutanenitrile* (**9a**).—Alkene **9** and TsI gave nitrile **9a** as a solid (80%), m.p. 104–107 °C (ethanol) (Found: C, 37.6; H, 3.5; I, 36.7; S, 9.0. $C_{11}H_{12}INO_2S$ requires: C, 37.84; H, 3.46; I, 36.34; S, 9.18%); ν(Nujol)/cm^{-1} 2260, 1600, 1290, 1145, 1090, 930, 820, 810, 770 and 560; δ_H(CDCl$_3$, 200 MHz) 7.80 (d, 2 H, *J* 8.3, Ar), 7.42 (d, 2 H, *J* 8.0, Ar), 4.60 (m, 1 H, *J* 10.2, 6.2, 4.5, 3.7, CHI), 3.81 (dd, 1 H, *J* 14.2, 10.2, CH$_2$Ts), 3.73 (dd, 1 H, *J* 14.2, 4.6, CH$_2$Ts), 3.62 (dd, 1 H, *J* 17.6, 6.3, CH$_2$CN), 3.37 (dd, 1 H, *J* 17.6, 3.7, CH$_2$CN) and 2.48 (s, 3 H, CH$_3$Ar); δ_C(CDCl$_3$, 200 MHz) 146.00 (Ar), 135.47 (Ar), 130.41 (Ar), 127.97 (Ar), 116.66 (CN), 63.85 (CH$_2$Ts), 29.38 (*C*H$_2$CN), 21.72 (CH$_3$Ar) and 6.68 (CI); *m*/*z* 222 (M − I, 13%), 155 (100), 139 (14), 91 (68) and 65 (38).

(E)- *and* (Z)-4-*Tosylbut*-2-*enenitrile* (**9b**).—Sulfone **9a** gave nitrile **9b** as a solid (77%, *E*:*Z* = 45:55) m.p. 69–71 °C (ethanol) (Found: C, 59.6; H, 5.1; N, 6.2; S, 14.7. $C_{11}H_{11}NO_2S$ requires: C, 59.71; H, 5.01; N, 6.33; S, 14.49%); ν(Nujol)/cm^{-1} 3075, 2240, 1635, 1600, 1305, 1180, 1150, 1090, 980, 910, 830, 740, 680, 595, 560 and 520; δ_H(CDCl$_3$, 200 MHz) 7.78 (d, 2 H, *J* 8.2, Ar, *E* or *Z*), 7.75 (d, 2 H, *J* 8.1, Ar, *Z* or *E*), 6.56 (m, 1 H, *J* 16.3, 10.9, 7.9, =CHCH$_2$, *E* and *Z*), 5.58 (dt, 1 H, *J* 10.9, 1.1, =CHCN, *Z*), 5.43 (dt, 1 H, *J* 16.3, 1.3, =CHCN, *E*), 4.16 (dd, 2 H, *J* 7.9, 1.0, CH$_2$Ts, *Z*), 3.93 (dd, 2 H, *J* 7.8, 1.2, CH$_2$Ts, *E*) and 2.48 (s, 3 H, CH$_3$Ar, *Z* and *E*); δ_C(CDCl$_3$, 300 MHz) 145.86 and 145.76 (Ar), 140.14 and 139.61 (=*C*HCH$_2$), 134.79 and 134.65 (Ar), 130.22 and 130.16 (Ar), 128.41 and 128.36 (Ar), 115.65 and 113.96 (CN), 108.02 and 107.00 (*C*HCN), 59.61 and 58.43 (CH$_2$Ts) and 21.73 (CH$_3$Ar); *m*/*z* 221 (M$^+$, 5%), 155 (56), 91 (100) and 65 (28).

3-*Iodo*-2,2-*dimethyl*-4-*tosylbutane* (**10a**).—Alkene **10** and TsI gave butane **10a** as a solid (91%), m.p. 77–79 °C (methanol) (Found: C, 42.3; H, 5.2; S, 8.5. $C_{13}H_{19}IO_2S$ requires: C, 42.63; H, 5.23; S, 8.75%); ν(Nujol)/cm^{-1} 1600, 1302, 1143, 1090, 910, 870, 750, 560 and 530; δ_H(CDCl$_3$, 300 MHz) 7.82 (d, 2 H, *J* 8.2, Ar), 7.39 (d, 2 H, *J* 8.0, Ar), 4.19 (t, 1 H, *J* 5.3, CHI), 3.72 (d, 2 H, *J* 5.4, CH$_2$Ts), 2.47 (s, 3 H, CH$_3$Ar) and 1.04 [s, 9 H, (CH$_3$)$_3$C]; δ_C(CDCl$_3$, 300 MHz) 145.16 (Ar), 136.03 (Ar), 129.94 (Ar), 128.59 (Ar), 63.34 (CH$_2$Ts), 36.09 and 35.93 (*C*Me$_3$ and *C*HI), 27.70 [C(*C*H$_3$)$_3$] and 21.71 (CH$_3$Ar); *m*/*z* 239 (M − I, 100%), 157 (73), 139 (80), 91 (22), 83 (28), 65 (18), 55 (34) and 41 (45).

(E)-3,3-*Dimethyl*-1-*tosylbut*-1-*ene* (**10b**).—Sulfone **10a** gave **10b** as a solid (58%), m.p. 50–52 °C (light petroleum, b.p. 60–80 °C) (Found: C, 65.5; H, 7.6; O, 13.3; S, 13.5. $C_{13}H_{18}O_2S$ requires C, 65.51; H, 7.61; O, 13.43; S, 13.45%); ν(Nujol)/cm^{-1} 3060, 1625, 1600, 1320, 1295, 1150, 1095, 985, 845, 820, 810, 765, 580 and 550; δ_H(CDCl$_3$, 300 MHz) 7.75 (d, 2 H, *J* 8.1, Ar), 7.33 (d, 2 H, *J* 7.8, Ar), 6.96 (d, 1 H, *J* 15.0, =CHC), 6.19 (d, 1 H, *J* 15.3, =CHTs), 2.44 (s, 3 H, CH$_3$Ar) and 1.08 [s, 9 H, (CH$_3$)$_3$C]; δ_C(CDCl$_3$, 300 MHz) 155.84 (=*C*HCMe$_3$), 144.13 (Ar), 137.82 (Ar), 129.86 (Ar), 127.57 (Ar), 126.73 (=CHTs), 34.06 (*C*Me$_3$), 28.34 [C(*C*H$_3$)$_3$] and 21.59 (CH$_3$Ar).

1-*Iodo*-2-*tosylethyl Acetate* (**11a**).—Alkene **11** and TsI gave **11a** as a solid (86%), m.p. 75–77 °C (ethanol) (Found: C, 35.7; H, 3.6; I, 34.8; O, 17.25; S, 8.7. $C_{11}H_{13}IO_4S$ requires C, 35.88; H, 3.56; I, 34.47; O, 17.38; S, 8.71%); ν(Nujol)/cm^{-1} 1770, 1750, 1600, 1320, 1220, 1200, 1160, 1145, 1095, 1025, 820, 770, 745, 540 and 520; δ_H(CDCl$_3$, 200 MHz) 7.74 (d, 2 H, J 8.3, Ar), 7.39 (d, 2 H, J 8.0, Ar), 7.09 (dd, 1 H, J 10.9, 1.8, CHI), 4.25 (dd, 1 H, J 14.8, 10.9, CH$_2$Ts), 3.88 (dd, 1 H, J 14.8, 1.8, CH$_2$Ts), 2.46 (s, 3 H, CH$_3$Ar) and 1.85 (s, 3 H, CH$_3$CO); δ_C(CDCl$_3$, 200 MHz) 167.44 (CO), 145.45 (Ar), 136.06 (Ar), 130.08 (Ar), 128.08 (Ar), 66.15 (CH$_2$Ts), 40.43 (*C*HI), 21.61 (CH$_3$Ar) and 20.65 (CH$_3$CO).

(E)-2-*Tosylvinyl Acetate* (**11b**).—Ester **11a** gave product **11b** as a solid (69%), m.p. 105–108 °C (ethanol) (Found: C, 54.7; H, 5.0; O, 27.0; S, 13.3. $C_{11}H_{12}O_4S$ requires C, 54.99; H, 5.03; O, 26.64; S, 13.34%). ν(Nujol)/cm^{-1} 3080, 1790, 1645, 1600, 1320, 1310, 1190, 1180, 1145, 970, 825, 795, 680, 590 and 550; δ_H(CDCl$_3$, 200 MHz) 8.33 (d, 1 H, J 12.1, =CHO), 7.78 (d, 2 H, J 8.3, Ar), 7.34 (d, 2 H, J 8.4, Ar), 6.27 (d, 1 H, J 12.2, CHTs) 2.44 (s, 3 H, CH$_3$Ar) and 2.22 (s, 3 H, CH$_3$CO); δ_C(CDCl$_3$, 300 MHz) 166.14 (CO), 147.63 (=CHO), 144.54 (Ar), 138.05 (Ar), 129.97 (Ar), 127.48 (Ar), 116.61 (=*C*HTs), 21.61 (CH$_3$Ar) and 20.43 (CH$_3$CO).

Competition Experiments.—Weighed quantities (0.2–0.4 mmol) of the two alkenes were placed in a Pyrex glass tube, covered by aluminium foil and 2.00 cm^3 of 1–2% of internal standard in the solvent to be used, followed by tosyl iodide (55 mg; 0.2 mmol) were added. The tube was stoppered, homogenized and maintained at 25.0 °C. The aluminium foil was removed and the orange solution irradiated under visible light for 15 min. The solution was analysed by GLC. For each pair of alkenes in competition about 10 runs were carried out, with different concentrations of the alkenes.

GLC Analysis.—Relative reactivities were determined using Varian 3700 and Tracor 565 instruments equipped with a flame ionization detector and coupled to SP 4290 and HP 3390 A electronic integrators, respectively. The chromatographic columns used were as follows: Column A: 10% Carbowax 1500, in Chromosorb W-HP 80/100 mesh (3 m × 6.35 mm). Column B: 3% OV 101 Chrom-HP, 80/100 mesh, 2 m × 3.18 mm. Column C: 3% SE 30 Supelcoport 2.09 m × 3.18 mm. Column D: 10% Carbowax 20 M, Chrom W-HP 2 m × 3.18 mm. Column E: 15% Silicon 200/50, 80/100 mesh, 1.52 × 3.18 mm. Column F: 3% OV 17 on gas chrom 100/120 mesh 2 m × 6.35 mm glass. The internal standards (and columns) used in the competition reactions 1–43 (Tables 3–5) were: CH$_2$Cl$_2$: 1(A), 2(A), 6(A), 10(A), 11(A), 14(A), 15(A); ClC$_6$H$_5$: 4(A), 5(B), 12(A), 13(C), 16(A), 40(D), 43(A); CCl$_4$: 8(A), 18(A); C$_6$H$_6$: 9(A), 17(A), 19(D), 20(A); *p*-ClC$_6$H$_4$Br: 7(B); BrC$_6$H$_5$: 22(D), 42(C); CH$_3$CN: 32(A); *o*-Cl$_2$C$_6$H$_4$: 31(E); CH$_3$C$_6$H$_5$: 21(F), 37(D), 38(D), 39(D); CH$_3$CO$_2$CH$_3$: 41(A).

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