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Free Radical Addition Reactions of Allylic Sulfones to Alkenes[1]

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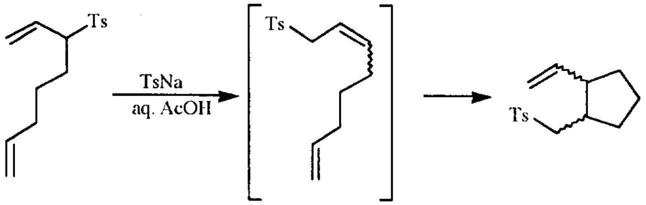
Abstract: Intermolecular radical reactions involving formal addition of the sulfonyl and allyl fragments of an allylic sulfone across the double bond of an alkene are described. Reactions are most successful when the allylic sulfone has an electron withdrawing group at the 2-position. Only monosubstituted alkenes give useful yields of adducts, though both electron withdrawing and electron donating substituents are effective. © 1997 Elsevier Science Ltd.

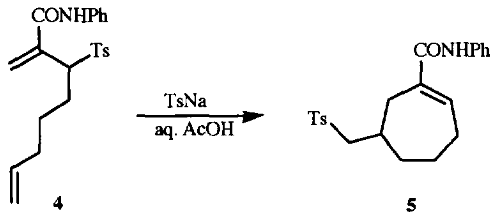
Introduction

Free radical reactions have become widely used in organic synthesis, often effecting selective transformations under mild conditions.[2] Of particular interest to synthetic chemists have been methods resulting in the formation of new carbon-carbon bonds.[3] The most commonly used procedures involve tin hydrides and typically a free radical chain is propagated by reaction of a tin radical with, for example, a halide, selenide, or thiocarbonyl compound, addition of the resulting carbon radical to a carbon carbon multiple bond, followed by abstraction of hydrogen resulting in reformation of the tin radical.[4] In an extension of this methodology, allylic stannanes have been used as the source of the tin radical, free radical allylation by an addition-elimination (S_H2') reaction replaces the hydrogen abstraction propagation step of the tin hydride procedure.[5]

Procedures involving stannanes suffer certain disadvantages, notably the toxicity of the tin residues and purification problems.[6] Investigations in our laboratory have been concerned with free radical addition-elimination reactions of allylic sulfones involving sulfonyl radicals in the propagation steps,[7] and we have previously described 1,3-rearrangement reactions of allylic sulfones[8] and cyclisations of suitably constituted unsaturated allylic sulfones[9] occurring *via* this type of process. Thus, upon treatment with sodium *p*-toluenesulfinate in aqueous acetic acid[10] sulfone **1** underwent 1,3-rearrangement to **2** followed by a favoured 5-*exo* cyclisation to give **3**.[11] In contrast, under similar conditions, sulfone **4** underwent cyclisation directly to give sulfone **5**.[12] These results were rationalised by considering that the electrophilic sulfonyl radical should add less readily to the electron deficient double bond of sulfone **4**, retarding the 1,3-rearrangement, while the nucleophilic alkyl radical (resulting from sulfonyl radical addition to the second, electron rich, double bond) should add more readily, enhancing the rate of the 7-*endo* cyclisation.



1 **2** **3**



4 **5**

The cyclisation reactions shown above involve the intramolecular addition of the sulfonyl and allyl groups of the allylic sulfone across the double bond of the alkene. We report here results of investigations into analogous intermolecular processes of the type outlined in Scheme 1. S_H2' reactions of allylic sulfones leading to carbon-carbon bond formation, in which organic halides,[13] organomercury compounds,[14] *N*-hydroxy-2-thiopyridone esters,[15] and ketones[16] serve as sources of carbon-centred radicals, have been reported by other workers.

6a R=OAc
6b R=$^nC_6H_{13}$
6c R=Ph
6d R=CO_2Me
6e R=CN

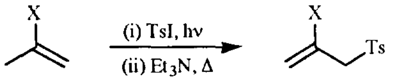
7f X=CO_2Me
7g X=CN
7h X=CONHPh
7i X=S*p*Tol
7j X=S(O)*p*Tol
7k X=Ts
7l X=NO_2
7m X=H
7n X=Me

8af R=OAc, X=CO_2Me
8bf R=$^nC_6H_{13}$, X=CO_2Me
8cf R=Ph, X=CO_2Me
8df R=CO_2Me, X=CO_2Me
8ef R=CN, X=CO_2Me
8ah R=OAc, X=CONHPh
8ak R=OAc, X=Ts

Scheme 1

Results and Discussion

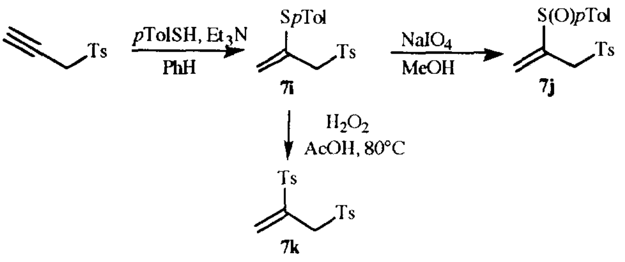
Considering the normal influence of substituent effects on free radical reactions[17] we considered that the addition process was more likely to be successful when the group X of the allylic sulfone **7** was electron withdrawing. We found that certain sulfones of this type (**7f-h**) could be prepared from methacrylate derivatives by addition of tosyl iodide followed by elimination of hydrogen iodide and *in situ* equilibration to the more stable βγ-unsaturated isomer (eq. 1).[18] Related preparations of vinylic and allylic sulfones have been described by other workers.[19] By a similar procedure, addition to methyl methacrylate of methanesulfonyl iodide followed by dehydroiodination / equilibration gave the allylic *methyl* sulfone **25**.



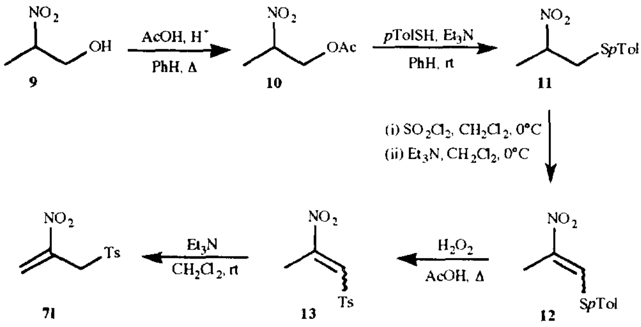
7f-h (1)

The *p*-tolylthio sulfone **7i**, prepared[20] by the base catalysed reaction of *p*-thiocresol with propargyl *p*-tolyl sulfone, was oxidised with either $NaIO_4$ (MeOH, 50°C) to give the sulfinyl sulfone **7j**, or with H_2O_2 (AcOH, 80°C) giving the bis-sulfone **7k**[21] (Scheme 2). Following unsuccessful attempts to iodosulfonylate 2-

nitropropene, the nitro-sulfone **7l** was prepared by the route shown in Scheme 3, involving Pummerer-type oxidation of thioether **11** and isomerisation of αβ-unsaturated sulfone **13** to the βγ-unsaturated sulfone **7l**. Although a variety of conditions were tried for the isomerisation reaction of **13** to **7l**, the reaction was low yielding (24%), presumably due to the instability of the product nitroalkene to the basic conditions.



Scheme 2



Scheme 3

Preliminary investigations of the addition reaction were conducted using sulfone **7f** and either vinyl acetate (**6a**) or oct-1-ene (**6b**) as the alkene. When the sulfone and excess alkene were heated together in carbon tetrachloride in the presence of 5mol% benzoyl peroxide (BPO) as initiator, formation of the desired adducts **8af** and **8bf** was observed in ^1H n.m.r. spectra taken of aliquots of the reaction mixtures. The reaction was qualitatively faster with vinyl acetate than with oct-1-ene, perhaps reflecting the greater facility of addition of the electrophilic sulfonyl radical to the more electron rich double bond. However, extended reaction times failed to achieve complete consumption of the starting sulfone **7f**, and decomposition of the products began to occur. A possible rationalisation was that the addition products **8** contain an electron deficient double bond which might suffer competing radical addition reactions when the concentration of **7f** was lowered as the reaction progressed. Based on this hypothesis, a reversal of the ratio of alkene/sulfone was tried, with the alkenes **6a** or **6b** being heated with 3 equivalents of **7f**, 5mol% BPO in carbon tetrachloride as before. Under these conditions (Method A) complete consumption of the starting alkenes was observed, with adducts **8af** and **8bf** being isolated in 66% and 62% yields respectively

Vinyl acetate **6a** was then used to compare the reactivities of the allylic sulfones **7f-n** in the addition reaction (Table 1). Many of the sulfones were insufficiently soluble in carbon tetrachloride for the reaction to be conducted under similar concentrations to those used for the reactions of **7f**, and in these cases $CDCl_3$ was substituted as the solvent. As expected, the addition was only successful when the group X of the allylic sulfone was electron withdrawing. While no addition was observed with the sulfoxide **7i**, the reactivity of the amide **7h** appeared to be marginal, with the slow appearance in the ^1H n.m.r. spectrum of signals tentatively assigned to the adduct **8ah**, which was not, however, isolated from the reaction mixture. No adduct was obtained from the attempted reaction of **7l-n** with vinyl acetate under similar conditions. The attempted addition of **7l** with vinyl acetate gave a complicated mixture of products, while **7m** and **7n** were recovered unchanged.

Table 1. Reaction of β-Substituted Allylic Sulfones with Vinyl Acetate

Sulfone	Conditions[a]	Adduct 8	Yield[b]
7f	BPO / CCl_4 / Δ / 6h	**8af**	66%
7g	BPO / $CDCl_3$ / Δ / 32h	**8ag**	77%
7h	BPO / $CDCl_3$ / Δ / 144h	**8ah**	c
7i	BPO / CCl_4 / Δ / 14h	-	-
7j	BPO / $CDCl_3$ / Δ / 32h	-	-
7k	BPO / $CDCl_3$ / Δ / 32h	**8ak**	48 %
7l	BPO / $CDCl_3$ / Δ / 32h	-	-
7m	BPO / CCl_4 / Δ / 32h	-	-
7n	BPO / CCl_4 / Δ / 24h	-	-

a. Alkene **6a** (1eq.), sulfones **7** (3eq.) under reflux in CCl_4 or $CDCl_3$, 0.05eq. BPO was added every 6h (reactions in CCl_4) or 16h (reactions in $CHCl_3$).

b. Isolated yield.

c. Adduct detected (low yield) by ^1H n.m.r. in the crude reaction mixture, but not isolated.

Sulfone **7f** was then used to compare the reactivities of various alkenes and of phenyl acetylene in the addition reaction. The results of these studies are summarised in Table 2. Adducts were isolated in all cases tried where the alkene was monosubstituted. The electronic influence of the group R in the alkene seems not to be as crucial to the success of the reaction as that of the group X in the allylic sulfone. However, when the alkene was disubstituted, only low yields of the desired adducts could be (tentatively) identified in the ^1H n.m.r .spectra of the crude reaction products. Since the addition is not successful with disubstituted alkenes, it appears that steric factors are important in determining the outcome of the reaction. With isopropenyl acetate **14** as the alkene, none of the desired adduct **15** was detected; however, a low yield (8%) of the dimer **16** of **7f** was isolated. Dimer **16** was observed by ^1H n.m.r. to be formed slowly when sulfone **7f** was heated in carbon tetrachloride in the presence of BPO, but was not observed upon heating in the absence of BPO. The formation of dimer **16** provides convincing evidence for a stepwise addition-elimination mechanism rather than a concerted mechanism for S_H2' reactions of allylic sulfones. The reaction of sulfone **7f** with phenyl acetylene **23** gave adduct **24** as a single isomer, the *Z* stereochemistry of which was confirmed in a nuclear Overhauser enhancement experiment. Column chromatography achieved only partial separation of the adduct **24** from the excess of sulfone **7f**, although a small quantity of pure material was isolated.

Table 2. Reaction of Sulfone 7f with Various Alkenes

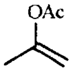
Alkene	Conditions[a]	Adduct	Yield
6a	BPO / Δ / 6 h	**8af**	66%[b]
6b	BPO / Δ / 12 h	**8bf**	62%[b]
6c	BPO / Δ / 8 h	**8cf**	58%[b]
6d	BPO / Δ / 8 h	**8df**	69%[b]
6e	BPO / Δ / 16 h	**8ef**	42%[b]
14	BPO / Δ / 16 h	-	-
17	BPO / Δ / 16 h	**18**	c
19	BPO / Δ / 12h	**20**	c
21	BPO / Δ / 18h	**22**	c
23	BPO / Δ / 32 h	**24**	70%[d]

a. Alkenes or phenylacetylene (1eq.), sulfone **7f** (2-3eq.) under reflux in CCl_4, 0.05eq. BPO was added every 6-8h.

b. Isolated yield.

c. Adduct detected (low yield) by ^1H n.m.r. in the crude reaction mixture, but not isolated.

d. Estimated yield.



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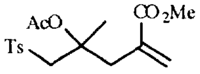

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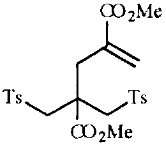

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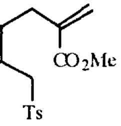

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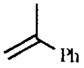

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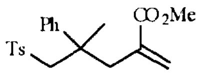

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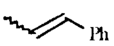

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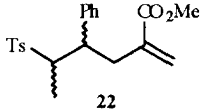

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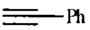

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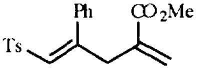
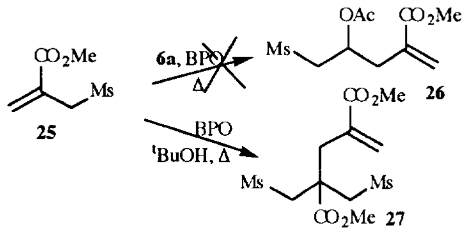


24

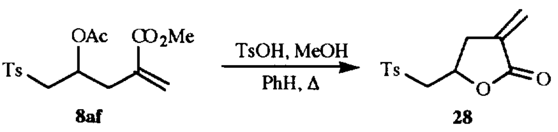
Under the standard conditions, only a low yield of adduct **18** was observed in the reaction of cyclohexene **17** with sulfone **7f**. However modification of the reaction conditions by changing the solvent to *t*-butanol and using excess alkene (3eq.) (Method B) allowed a fair yield (36%) of adduct **18** to be isolated as a 7:1 mixture of diastereoisomers. It is noteworthy that the use of excess alkene was found to be unsatisfactory when carbon tetrachloride was used as the solvent. For comparison, the reaction of 1-octene with sulfones **7f** and **7h** was also attempted under the modified conditions: sulfone **7f** gave adduct **8bf** in 43% yield, while sulfone **7h** gave adduct **8bh** in 66% yield.

To explore further the scope of the addition reaction, the addition of the allylic methyl sulfone **25** with vinyl acetate **6a** was attempted. Under the standard conditions (Method A), using either carbon tetrachloride or *t*-butanol as the solvent, complicated mixtures of products were obtained with no indication, in the ^{1}H n.m.r. spectra of the crude product, of formation of the desired adduct **26**. Sulfone **25** was found to be unstable when heated with BPO in the absence of alkene, undergoing rapid decomposition in either carbon tetrachloride or *t*-butanol as solvent, although no decomposition occurred upon heating in solvent in the absence of BPO. When sulfone **25** was heated with BPO in *t*-butanol, the major decomposition product was tentatively identified as the dimer **27**, by comparison of the ^{1}H n.m.r. spectra of the crude product with that of dimer **18**. Kinetic studies performed by Wagner and co-workers[22] suggest that β-arylsulfonyl alkyl radicals may undergo β-scission with loss of a sulfonyl radical approximately 15 times faster than β-alkylsulfonyl alkyl radicals. This result may provide a rationalisation of the reactivity of sulfone **25**: radicals resulting from addition to sulfone **25** are longer lived, and thus have a greater likelihood of participating in competing reactions than analogous radicals from addition to sulfone **7f**.



Scheme 4

As an illustration of the potential synthetic utility of the addition reaction of allylic sulfones and alkenes, adduct **8af** was converted, upon treatment with catalytic amounts of *p*-toluenesulfonic acid and methanol under reflux in benzene, into the α-methylene-γ-lactone **28** (eq. 2). The two step synthesis of **28** from vinyl acetate represents a concise construction of this important lactone functionality.[23]



(2)

Conclusion

The addition reaction described in this paper would most likely find use as a method for extending alkene substrates, with the allylic sulfone as a reagent. Thus, the conditions using excess allylic sulfone are likely to prove more useful. Using the procedures described, reasonable yields of adducts of activated allylic sulfones with terminal alkenes can be obtained. Following publication of the preliminary account of the present work, a small number of reports of related free radical procedures involving allylic sulfones have appeared. Bertrand[24] and Chuang[25] and co-workers have described addition of activated allylic sulfones to 1,5-dienes, proceeding with cyclisation of the intermediate radical resulting from addition of the sulfonyl radical to the first double bond of the diene. Quiclet-Sire and Zard[26] have described additions to alkenes involving allylic sulfones where the intermediate sulfonyl radical can readily undergo loss of sulfur dioxide to give a stabilised (e.g. allyl, arylmethyl) carbon-centred radical, resulting in overall addition to the alkene with the formation of two new carbon-carbon bonds. Finally, Hosomi and co-workers[27] have recently described addition reactions of allylic stannanes to alkenes.

Experimental.

^{1}H n.m.r. spectra were recorded using Varian Gemini-200 (200MHz), Brucker WH300 (300MHz) , or Brucker AM500 (500MHz) spectrometers; ^{13}C n.m.r. spectra were recorded using Varian Gemini-200 (50MHz), Brucker AM250 (63MHz), or Brucker AM500 (126MHz) spectrometers. Chemical shifts are quoted in p.p.m. downfield fromTMS. Solvents and reagents described as 'dry' were purified by standard methods.[28] Benzoyl peroxide (BPO) was precipitated from $CHCl_3$ with cold MeOH. "Light petroleum" refers to the fraction boiling at 30-40°C unless indicated. Removal of solvents was performed under reduced pressure on a rotary evaporator.

CAUTION Allylic sulfones of the type 7 with an electron withdrawing group at the β-position have been observed by both ourselves and other workers[29] to be potent skin irritants. Precautions should therefore to be taken to avoid skin contact of these compounds.

General Procedure for the Preparation of β-Substituted Allylic Sulfones from *p*-Toluenesulfonyl Iodide and Methacrylic Acid Derivatives. A saturated solution of iodine (1.5eq.) in ethanol was added dropwise, in the dark, to a stirred solution of sodium *p*-toluenesulfinate dihydrate (1.5eq.) in water (ca. 0.1M solution). The yellow precipitate was collected, washed with water, dissolved in carbon tetrachloride, dried ($MgSO_4$). and filtered. The methacrylic acid derivative (purified of inhibitor either by distillation or by washing a solution in carbon tetrachloride with dilute aqueous sodium hydroxide) was added to the resulting solution which was then stirred at 20°C in the light until no starting acid derivative was visible by t.l.c. The solvent was evaporated and the residue was redissolved in carbon tetrachloride. Triethylamine (4eq.) was added, then the resulting mixture was heated under reflux for 15h. After cooling the solution was washed with dilute aqueous hydrochoric acid and water, then dried ($MgSO_4$), filtered, and evaporated to give the crude sulfone. The following sulfones were prepared by this method:

2-[(4-Methylphenylsulfonyl)methyl]propenoic acid methyl ester (7f). Prepared from methyl methacrylate (7.5g), iodine (30g) and sodium *p*-toluenesulfinate dihydrate (25g). Filtration of a solution of the crude sulfone in dichloromethane through a plug of silica gel, followed by evaporation gave sulfone **7f** (13g, 69%) as plates; m.p. 41-42.5°C (from dichloromethane / *n*-pentane); (Found: C, 56.65; H, 5.6. Calc. for $C_{12}H_{14}O_4S$: C, 56.7; H, 5.55%.); ν_{max}($CHCl_3$) 1730, 1335, 1150cm^{-1}; δ_H(200MHz; $CDCl_3$) 2.45 (3H, s, $ArC\underline{H}_3$), 3.60 (3H, s, $C\underline{H}_3O$), 4.14 (2H, s, $C\underline{H}_2SO_2$), 5.89 (1H, s, $=C\underline{H}$), 6.50 (1H, s, $=C\underline{H}$), 7.33 (2H, d, J=8Hz, Ar), 7.73 (2H, d, J=8Hz, Ar); *m/z* (DCI, NH_3) 272 (100%, MNH_4^+), 253 (32%, MH^+).

2-[(4-Methylphenylsulfonyl)methyl]propenonitrile (7g). Prepared from methacrylonitrile (0.1g), iodine (0.68g) and sodium *p*-toluenesulfinate dihydrate (25g). Recrystallisation from dichloromethane / *n*-pentane gave sulfone **7g** (0.17g, 52%) as needles, m.p. 109-110°C; (Found: C, 59.7; H, 4.85. Calc. for $C_{11}H_{11}NO_2S$: C, 59.7; H, 5.0%.); ν_{max}($CHCl_3$) 2235, 1600, 1330, 1155cm^{-1}; δ_H(200MHz; $CDCl_3$) 2.49 (3H, s, $ArC\underline{H}_3$), 3.92 (2H, s, $C\underline{H}_2$), 6.02 (1H, s, $=C\underline{H}$), 6.22 (1H, s, $=C\underline{H}$), 7.41 (2H, d, J=8Hz, Ar), 7.80 (2H, d, J=8Hz, Ar); δ_C(63MHz; $CDCl_3$) 21.5 (q, $Ar\underline{C}H_3$), 59.7 (t, $\underline{C}H_2SO_2$), 111.4 (s, Ar, $\underline{C}=CH_2$ or $\underline{C}N$), 116.5 (s, Ar, $\underline{C}=CH_2$ or $\underline{C}N$), 128.5 (d, Ar), 130.0 (d, Ar), 134.3 (s, Ar, $\underline{C}=CH_2$ or $\underline{C}N$), 139.3 (t, $CH=\underline{C}H_2$), 145.7 (s, Ar, $\underline{C}=CH_2$ or $\underline{C}N$); *m/z* (CI, NH_3) 239 (100%, MNH_4^+).

2-[(Methylsulfonyl)methyl]propenoic acid methyl ester (25). Solutions of sodium methanesulfinate[30] (6.6g, 65mmol) in water (115ml), and iodine (11.0g, 43mmol) in dichloromethane (230ml) were vigorously shaken together in a separating funnel, and the organic layer was quickly separated, dried ($MgSO_4$), and filtered. Methyl methacrylate (4.6ml, 43mmol) was added, and the solution was stirred for 15min under irradiation from a 275W bulb at 15cm. The resulting solution was washed with aqueous sodium thiosulfate and water, then dried ($MgSO_4$), filtered, and evaporated. The residue was recrystallised from dichloromethane / light petroleum to give the 2-iodo-2-methyl-3-methylsulfonylpropenoic acid methyl ester (9.0g, 29mmol, 67%); m.p.92-95°C (from dichloromethane / *n*-pentane); (Found: C, 23.65; H, 3.45. $C_6H_{11}O_4SI$ requires: C, 23.55. H, 3.65%.); ν_{max}(CCl_4) 1730, 1325, 1140cm^{-1}; δ_H(300MHz; $CDCl_3$) 2.44 (3H, s, $C\underline{H}_3$), 2.98 (3H, s, $C\underline{H}_3SO_2$), 3.85 (1H, d, J=14Hz, $C\underline{H}SO_2$), 3.86 (3H, s, $C\underline{H}_3O$), 4.46 (1H, d, J=14 Hz, $C\underline{H}SO_2$). Triethylamine (5ml, 3.6g, 36mmol) was added to a solution of the iodo-sulfone (3.1g, 10.1mmol) in dichloromethane (35ml) which was then heated under reflux for 8h. After cooling, the solution was washed with dilute aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and aqueous sodium thiosulfate, then dried ($MgSO_4$), filtered and evaporated. The resulting dark oil was crystallised from methanol / light petroleum to give the 2-[(methylsulfonyl)methyl]propenoic acid methyl ester (**25**). (1.35g, 7.6mmol, 75%); m.p. 64-66°C (from methanol / *n*-pentane); (Found: C, 40.35; H, 5.9. $C_6H_{10}O_4S$ requires: C, 40.45. H, 5.65%.); ν_{max}($CHCl_3$) 1720, 1630, 1315, 1140cm^{-1}; δ_H(300MHz; $CDCl_3$) 2.91 (3H, s, $C\underline{H}_3SO_2$), 3.84 (3H, s, CH_3O), 4.07 (2H, s, $C\underline{H}_2SO_2$), 6.18 (1H, s, $=C\underline{H}$), 6.65 (1H, s, $=C\underline{H}$); δ_C(50MHz; $CDCl_3$) 40.2 (q, $\underline{C}H_3SO_2$), 52.5 (q, $\underline{C}H_3O$), 56.2 (t, $\underline{C}H_2SO_2$), 128.8 (s, $\underline{C}=CH_2$), 134.2 (t, $C=\underline{C}H_2$), 165.9 (s, $\underline{C}=O$); *m/z* (Probe CI, NH_3) 196 (100%, MNH_4^+).

2-(4-Methylphenylsulfinyl)-3-(4-methylphenylsulfonyl)-1-propene (7j). To a solution of the 3-(4-methylphenylsulfonyl)-2-(4-methylphenylthio)-1-propene (**7i**)[31] (10.0g, 31mmol) in methanol (1l), a solution of sodium metaperiodate (6.7g, 31mmol) in water (100ml) was added in portions, with agitation between the addition of successive portions. The mixture was then left at 50°C for 60h. The solvent was evaporated, then the residue was partitioned between water (200ml) and dichloromethane (200ml), the layers were separated, and the aqueous layer was extracted with further dichloromethane (100ml). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue (9.7g) was recrystallised from ethanol to give 2-(4-methylphenylsulfinyl)-3-(4-methylphenylsulfonyl)-1-propene (**7j**) (7.4g, 22mmol, 71%) as needles; m.p. 135.5-143°C; (Found: C, 61.05; H, 5.5. $C_{17}H_{18}O_3S_2$ requires: C, 61.05; H, 5.45%.); ν_{max}($CHCl_3$) 1600, 1495, 1325, 1150, 1050cm^{-1} (Ar); δ_H(300MHz; $CDCl_3$) 2.41 (3H, s, $\mathrm{ArC\underline{H}_3}$), 2.47 (3H, s, $\mathrm{ArC\underline{H}_3}$), 3.49 (1H, d, J=15Hz, $\mathrm{C\underline{H}S}$), 3.92 (1H, d, J=15Hz, $\mathrm{C\underline{H}S}$), 6.06 (1H, s, $\mathrm{=C\underline{H}}$), 6.31 (1H, s, $\mathrm{=C\underline{H}}$), 7.27 (2H, d, J=8Hz, Ar), 7.35 (2H, d, J=8Hz, Ar), 7.42 (2H, d, J=8Hz, Ar), 7.70 (2H, d, J=8Hz, Ar); δ_C(50MHz; $CDCl_3$) 21.2 (q, $\mathrm{Ar\underline{C}H_3}$), 21.5 (q, $\mathrm{Ar\underline{C}H_3}$), 54.3 (t, $\mathrm{\underline{C}H_2SO_2}$), 123.9 (t, $\mathrm{C{=}\underline{C}H_2}$), 125.7 (d, Ar), 128.7 (d, Ar), 130.0 (d, Ar), 130.3 (d, Ar), 134.7 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$), 138.1 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$), 142.8 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$), 143.3 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$), 145.5 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$); *m/z* (Probe CI, NH_3) 335 (100%, MH^+), 352 (10%, MNH_4^+).

2,3-Bis(4-methylphenylsulfonyl)propene (7k). 3-(4-Methylphenylsulfonyl)-2-(4-methylphenylthio)propene (**7i**) (15.0g, 47mmol) was dissolved in acetic acid (60ml). Aqueous hydrogen peroxide (30% w/w; 60ml) was added, and the solution was stirred at 80°C for 2h. After cooling, the solution was poured onto crushed ice (150ml), and the solid which precipitated (12.4g) was collected by filtration and dried under vacuum. Recrystallisation from ethanol gave 2,3-bis(4-methylphenylsulfonyl)propene (**7k**) (7.4g, 21mmol, 45%); m.p. 149-158°C (lit.[32] 155.5-157°C); ν_{max}($CHCl_3$) 1600, 1320, 1155, 1140cm^{-1}; δ_H(200MHz; $CDCl_3$) 2.46 (6H, s, $\mathrm{2xArC\underline{H}_3}$), 4.04 (2H, s, $\mathrm{C\underline{H}_2S}$), 6.51 (1H, d, J=1Hz, $\mathrm{=C\underline{H}}$), 6.66 (1H, s, $\mathrm{=C\underline{H}}$), 7.29 (4H, d, J=8Hz, Ar), 7.62 (4H, 2d, both J=8Hz, Ar); δ_C(50MHz; $CDCl_3$) 21.5 (q, $\mathrm{2xAr\underline{C}H_3}$), 54.0 (t, $\mathrm{\underline{C}H_2SO_2}$), 128.5 (d, Ar), 128.6 (d, Ar), 129.9 (d, Ar), 130.1 (d, Ar), 130.6 (t, $\mathrm{C{=}\underline{C}H_2}$), 134.8 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$), 139.9 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$), 145.3 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$), 145.5 (s, Ar, or $\mathrm{\underline{C}{=}CH_2}$); *m/z* (Probe CI, NH_3) 214 (100%), 368 (30%, MNH_4^+).

2-Nitropropan-1-ol (9). The nitro-alcohol was obtained from nitroethane and aqueous formaldehyde in 80 % yield after distillation using a method analogous to that used by Feuer and Miller[33] for the preparation of 2-nitrobutan-1-ol; b.p. 98-100°C at 11mmHg (lit.[34] 79-80°C at 5mmHg); ν_{max}(CCl_4) 3615, 1360cm^{-1}; δ_H(200MHz; $CDCl_3$) 1.47 (3H, d, J=7Hz, $\mathrm{C\underline{H}_3}$), 3.32 (1H, brs, $\mathrm{O\underline{H}}$), 3.83 (1H, dd, J=12, 4Hz, $\mathrm{C\underline{H}O}$), 3.93 (1H, dd, J=12, 8Hz, $\mathrm{C\underline{H}O}$), 4.65 (1H, m, $\mathrm{C\underline{H}N}$).

2-Nitro-1-propyl Acetate (10). 2-Nitropropan-1-ol (52.6g, 0.50mol), acetic acid (32.4g, 0.54mol), and conc. sulfuric acid (0.25ml) were dissolved in benzene (100ml). The solution was heated under reflux with collection of using a Dean and Stark separator. After 4h the benzene was evaporated and distillation of the residue then gave 2-nitro-1-propyl acetate (69.6g, 0.47mol, 94%) as an oil; b.p.103-104°C at 21mmHg; ν_{max}(CCl_4) 1755, 1360,cm^{-1}; δ_H(200MHz; $CDCl_3$) 1.55 (3H, d, J=12Hz, C$\underline{H}_3$), 2.05 (3H, s, C$\underline{H}_3$CO), 4.39 (2H, d, J=6Hz, C$\underline{H}_2$O), 4.78 (1H, m, C$\underline{H}$N).

1-(4-Methylphenylthio)-2-nitropropane (11). Triethylamine (30ml, 21.8g, 215mmol) was added dropwise over 30min to a solution containing 2-nitro-1-propyl ethanoate (25.0g; 170mmol) and *p*-thiocresol (23.0g, 185mmol) were dissolved in benzene (250ml), stirred at 0°C. The mixture was then allowed to warm to 18 °C and stirred for a further 2h. The solution was washed with dilute aqueous hydrochloric acid (250ml), aqueous sodium hydroxide (2.0M, 250ml), water (250ml), and brine (250ml), then dried ($MgSO_4$), filtered, and evaporated to give 1-(4-methylphenylthio)-2-nitropropane (**11**).(35.8g, 169mmol, 99%) as a yellow oil. Purification of a small sample by flash chromatography using ether / light petroleum (1:20v/v) as the eluent gave a pale oil; (Found: C, 56.75; H, 6.3. $C_{10}H_{11}NO_2S$ requires: C, 56.85; H, 6.2%.); ν_{max}(CCl_4) 1495, 1360cm^{-1}; δ_H(300MHz; $CDCl_3$) 1.62 (3H, d, J=7Hz, C$\underline{H}_3$), 2.35 (3H, s, ArC$\underline{H}_3$), 3.08 (1H, dd, J=14, 7Hz, C$\underline{H}$S), 3.44 (1H, dd, J=14, 7Hz, C$\underline{H}$S), 4.57 (1H, m, C$\underline{H}$N), 7.15 (2H, d, J=8Hz, Ar), 7.34 (2H, d, J=8Hz, Ar).

1-(4-Methylphenylthio)-2-nitropropene (12). Sulfuryl chloride (15ml, 20.3g, 150mmol) was added cautiously to a solution of 1-(4-Methylphenylthio)-2-nitropropane (**11**) (30.0g, 142mmol) at 0°C. After 5min, when effervescence had stopped, and the solvent and excess sulfuryl chloride were evaporated. The residue was redissolved in dichloromethane (150ml), and the solution was stirred at 0°C, then triethylamine (30ml; 21.8g; 215mmol) was added. After 5min, the solution was washed with dilute aqueous hydrochloric acid (200ml), saturated aqueous sodium bicarbonate (200ml), and water (200ml), then dried ($MgSO_4$), filtered, and evaporated to give a crude mixture of the *E* and *Z* isomers of 1-(4-methylphenylthio)-2-nitropropene (**12**) (28.9g; 138mmol; 97%) as a dark oil. Purification of a small sample by flash chromatography using ether / light petroleum (1:20 v/v) as eluent gave the separate isomers. *E* isomer: (Found: C, 57.1; H, 5.1. $C_{10}H_9NO_2S$ requires: C, 57.4, H, 5.3%.); ν_{max}(CCl_4) 3060, 1615, 1495, 1320cm^{-1} (NO_2); δ_H(300MHz; $CDCl_3$) 2.27 (3H, s, C$\underline{H}_3$), 2.39 (3H, s, ArC$\underline{H}_3$), 7.23 (2H, d, J=8Hz, Ar), 7.39 (2H, d, J=8Hz, Ar), 8.15 (1H, s, =C$\underline{H}$). *Z* isomer: m.p. 90-93°C (yellow plates from ether / *n*-pentane); (Found: C, 57.3; H, 5.2. $C_{10}H_9NO_2S$ requires: C, 57.4, H, 5.3%.); ν_{max}(CCl_4) 3035, 1610, 1495, 1315cm^{-1}; δ_H(300MHz; $CDCl_3$) 2.27 (3H, s, C$\underline{H}_3$), 2.40 (3H, s, ArC$\underline{H}_3$), 7.23 (2H, d, J=8Hz, Ar), 7.27 (1H, s, =C$\underline{H}$), 7.42 (2H, d, J=8Hz, Ar).

1-(4-Methylphenylsulfonyl)-2-nitropropene (13). A solution containing crude 1-(4-methylphenylthio)-2-nitropropene (**12**) (28.8g, 138mmol), aqueous hydrogen peroxide (30% w/w; 75ml) and acetic acid (150ml) was heated under reflux for 1h. After cooling, the solution was poured onto crushed ice (250ml), then extracted with ether (3x250ml). The combined extracts were washed with water (1l), dilute aqueous hydrochloric acid (250ml) aqueous sodium metabisulfite (1M; 250ml), water (250ml), and brine (250ml), then dried ($MgSO_4$), filtered and evaporated to give a yellow solid (25.8g) which was recrystallised from ether / light petroleum to give the 1-(4-methylphenylsulfonyl)-2-nitropropene (**13**) (19.6g, 81mmol, 59%) as a mixture of isomers. The isomers could be separated by dry column flash chromatography using dichloromethane / light petroleum (1:1v/v) as the eluant. *E* isomer: m.p. 82-84°C (needles from ether / *n*-pentane); (Found: C, 49.7; H, 4.65. $C_{10}H_{11}NO_4S$ requires: C, 49.8; H, 4.6%.); $\nu_{max}(CCl_4)$ 1660, 1600, 1495, 1340 , 1330, 1160cm^{-1}; δ_H(300MHz; $CDCl_3$), 2.49 (3H, s, ArC$\underline{H}_3$), 2.67 (3H, d, J=1Hz, C$\underline{H}_3$), 7.43 (2H, d, J=8Hz, Ar), 7.53 (1H, d, J=1Hz, =C$\underline{H}$), 7.84 (2H, d, J=8Hz, Ar). *Z* isomer: m.p. 112- 117°C (needles from ether / *n*-pentane); (Found: C, 49.85; H, 4.8. $C_{10}H_{11}NO_4S$ requires: C, 49.8; H, 4.6%.); $\nu_{max}(CHCl_3)$ 1655, 1595, 1365, 1340, 1155cm^{-1}; δ_H(300MHz; $CDCl_3$) 2.32 (3H, d, J=1Hz, C$\underline{H}_3$), 2.48 (3H, s, ArC$\underline{H}_3$), 6.21 (1H, d, J=1Hz, =C$\underline{H}$), 7.40 (2H, d, J=8Hz, Ar), 7.85 (2H, d, J=8Hz, Ar).

3-(4-Methylphenylsulfonyl)-2-nitropropene (7l). Triethylamine(5ml, 3.6g, 36mmol) was added all at once to a vigorously stirred solution of the 1-(4-methylphenylsulfonyl)-2-nitropropene (**13**) (5.0g, 24mmol) in dichloromethane (500ml) at 18°C. After 10min, the solution was immediately washed with aqueous hydrochloric acid (10%w/v; 1l), dried ($MgSO_4$), and filtered through chromatographic silica gel. The solvent was evaporated, without heating, under reduced pressure, and the residue was subjected to dry column flash chromatography using dichloromethane / light petroleum (1:1v/v) as the eluant which gave the 3-(4-methylphenylsulfonyl)-2-nitropropene (**7l**) (1.23g, 5.8mmol, 24%); m.p. 98-116°C (from dichloromethane / *n*-pentane); (Found: C, 49.6; H, 4.5. $C_{10}H_{11}NO_4S$ requires: C, 49.8; H, 4.6%.); $\nu_{max}(CHCl_3)$ 1600, 1540, 1345, 1330, 1150cm^{-1}; δ_H(300MHz; $CDCl_3$) 2.47 (3H, s, ArC$\underline{H}_3$), 4.47 (2H, s, C$\underline{H}_2$), 6.07 (1H, d, J=2Hz, =C$\underline{H}$), 6.83 (1H, d, J=2Hz, =C$\underline{H}$), 7.37 (2H, d, J=8Hz, Ar), 7.76 (2H, d, J=8Hz, Ar); δ_C(125MHz; $CDCl_3$) 21.67 (Ar$\underline{C}H_3$), 55.76 ($\underline{C}H_2S$), 125.21 (=$\underline{C}H_2$), 128.54, 130.10, and 134.81 (Ar), 145.82 and 146.82 (Ar and =C-NO_2).

Reaction of Allylic Sulfones with Alkenes. Method A. A solution of the allylic sulfone (2.0mmol), the alkene (0.67mmol), and benzoyl peroxide (8mg, 33μmol, 5mol%) in a suitable solvent ($CDCl_3$ or CCl_4, 2.5ml) was heated under reflux until the reaction was complete. Where prolonged reaction times were necessary, portions of fresh benzoyl peroxide (8mg) were added periodically during the reaction time. The solvent was removed, and the residue was subjected to flash chromatography to separate the adduct.

The following sulfones were prepared by this method:

4-Acetoxy-2-methylene-5-(4-methylphenylsulfonyl)pentanoic acid, methyl ester (8af). Prepared by the reaction of 2-[(4-methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7f**).with vinyl acetate (**6a**). The reaction was complete after 6h under reflux in carbon tetrachloride. 4-Acetoxy-2-methylene-5-(4-methylphenylsulfonyl)pentanoic acid, methyl ester **8af** (66%) was obtained after flash chromatography using ether / light petroleum (3:2 v/v) as the eluant; m.p. 88-91°C (from ether / *n*-pentane); (Found: C, 56.25; H, 5.95. $C_{16}H_{20}O_6S$ requires: C, 56.45; H, 5.95%.); ν_{max} (CCl_4) 1750, 1725, 1630, 1600, 1495, 1330 , 1155cm^{-1}; δ_H(300MHz; $CDCl_3$) 1.78 (3H, s, C$\underline{H}_3$.CO), 2.46 (3H, s, ArC$\underline{H}_3$), 2.57 (1H, dd, J=14, 7Hz, 3-C$\underline{H}$), 2.81 (1H, dd, J=14, 5Hz, 3-C$\underline{H}$), 3.33 (1H, dd, J=15, 4Hz, 5-C$\underline{H}$), 3.43 (1H, dd, J=15, 8Hz, 5-C$\underline{H}$), 3.74 (3H, s, $C\underline{H}_3O$), 5.41 (1H, m, 4-C$\underline{H}$), 5.63 (1H, d, J=1Hz, =C$\underline{H}$), 6.26 (1H, d, J=1Hz, =C$\underline{H}$), 7.37 (2H, d, J=8Hz, Ar), 7.79 (2H, d, J=8Hz, Ar); δ_C(126MHz; $CDCl_3$) 20.5 (q, Ar$\underline{C}H_3$, or $\underline{C}H_3CO$), 21.6 (q, Ar$\underline{C}H_3$, or $\underline{C}H_3CO$), 36.4 (t, C=C$\underline{C}H_2$), 52.1 (q, $\underline{C}H_3O$), 58.8 (t, $\underline{C}H_2SO_2$), 66.9 (d, $\underline{C}$HOAc), 128.3 (d, Ar), 128.9 (t, C=$\underline{C}H_2$), 129.9 (d, Ar), 135.1 (s, Ar or $\underline{C}=CH_2$), 136.7 (s, Ar or $\underline{C}=CH_2$), 144.9 (s, Ar or $\underline{C}=CH_2$), 166.7 (s, $\underline{C}$=O), 169.6 (s, $\underline{C}$=O); *m/z* (Probe CI, NH_3) 150 (100%), 358 (50%, MNH_4^+).

4-Acetoxy-2-methylene-5-(4-methylphenylsulfonyl)pentanonitrile (8ag). Prepared by the reaction of 2-[(4-methylsulfonyl)methyl]propenonitrile (**7g**) with vinyl acetate (**6a**). Fresh benzoyl peroxide having been added after 16h and the reaction was complete after 32h under reflux in chloroform-*d*. Flash chromatography using dichloromethane then ether / dichloromethane (1:10 v/v) as the eluant gave 4-acetoxy-2-methylene-5-(4-methylphenylsulfonyl)pentanonitrile (**8ag**) (77%); m.p. 131-133.5°C (from ether / *n*-pentane); (Found: C, 58.55; H, 5.5. $C_{15}H_{17}NO_4S$ requires: C, 58.6; H, 5.6%.); ν_{max}($CHCl_3$) 2230, 1750, 1600, 1495, 1325, 1145cm^{-1}; δ_H(300MHz; $CDCl_3$) 1.91 ($C\underline{H}_3CO$), 2.48 (3H, s, ArC$\underline{H}_3$), 2.69 (1H, dd, J=15, 7Hz, 3-C$\underline{H}$), 2.85 (1H, dd, J=15, 5Hz, 3-C$\underline{H}$), 3.33 (1H, dd, J=15, 6Hz, 5-C$\underline{H}$), 3.47 (1H, dd, J=15, 6Hz, 5-C$\underline{H}$), 5.34 (1H, m, 4-C$\underline{H}$), 5.90 (1H, s, =C$\underline{H}$), 6.04 (1H, s, =C$\underline{H}$) 7.40 (2H, d, J=8Hz, Ar), 7.80 (2H, d, J=8Hz, Ar).

4-Acetoxy-2,5-bis(4-methylphenylsulfonyl)-1-pentene (8ak). Prepared by the reaction of 2,3-bis(4-methylphenylsulfonyl)propene (**7k**) with vinyl acetate (**6a**). The reaction was complete after 32h under reflux in chloroform-*d* with fresh benzoyl peroxide having been added after 16h. After the solvent had been removed under reduced pressure, ether / light petroleum (3:1 v/v) was added, and the mixture was boiled briefly then filtered. The solution was then subjected to flash chromatography using ether / light petroleum (3:1 v/v) as the eluant, which gave 4-acetoxy-2,5-bis(4-methylphenylsulfonyl)-1-pentene (**8ak**). (48%); (Found: C,57.75; H,5.5. $C_{21}H_{24}O_6S_2$ requires: C,57.75; H,5.55%.); ν_{max} (CCl_4) 1750, 1600, 1495, 1325, 1145cm^{-1}; δ_H(300MHz; $CDCl_3$) 1.82 ($C\underline{H}_3CO$), 2.46 and 2.47 (6H, 2s, 2xArC$\underline{H}_3$), 2.61 (1H, dd, J=15,7Hz, 3-C$\underline{H}$), 2.75 (1H, dd, J=16,6Hz, 3-C$\underline{H}$), 3.29 (1H, dd, J=15,5Hz, 5-C$\underline{H}$), 3.38 (1H, dd, J=15,7Hz, 5-C$\underline{H}$), 5.35 (1H, m, 4-C$\underline{H}$), 5.84 (1H, d, J=1Hz, =C$\underline{H}$), 6.42 (1H, s, =C$\underline{H}$), 7.37 (4H, 2d, Ar), 7.77 (4H, 2d, Ar).

2-Methylene-4-[(4-methylphenylsulfonyl)methyl]decanoic acid, methyl ester (8bf). Prepared by the reaction of 2-[(4-methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7f**) with 1-octene (**6b**). Fresh benzoyl peroxide was added after 6h and the reaction was complete after 12h under reflux in carbon tetrachloride. Flash chromatography using ether / light petroleum (1:2 v/v) as the eluant gave 2-methylene-4-[(4-methylphenylsulfonyl)methyl]decanoic acid, methyl ester (**8bf**). (63%) as an oil which could be crystallised from light petroleum (b.p. 40-60°C); m.p. 22°C [from light petroleum (b.p. 40-60°C)]; (Found: C, 65.7; H, 8.2. $C_{20}H_{30}O_4S$ requires: C, 65.55; H, 8.25%.); ν_{max}(CCl_4) 1725, 1630, 1600, 1320, 1150cm^{-1}; δ_H(300MHz; $CDCl_3$) 0.88 (3H, t, J=7Hz, 10-C$\underline{H}_3$), 1.13-1.57 (10H, m, 5-C$\underline{H}_2$, 6-C$\underline{H}_2$, 7-C$\underline{H}_2$, 8-C$\underline{H}_2$, 9-C$\underline{H}_2$), 2.33 (1H, dd, J=14, 8Hz, 3-C$\underline{H}$), 2.46 (3H, s, ArC$\underline{H}_3$), 2.47 (1H, dd, J=14, 6Hz, 3-C$\underline{H}$), 2.99 (1H, dd, J=14, 6Hz, C$\underline{H}$S), 3.05 (1H, dd, J=14, 5Hz, C$\underline{H}$S), 3.70 (3H, s, $C\underline{H}_3O$), 5.53 (1H, s, =C$\underline{H}$), 6.21 (1H, s, =C$\underline{H}$), 7.35

(2H, d, J=8Hz, Ar), 7.77 (2H, d, J=8Hz, Ar); δ_C(125MHz; $CDCl_3$) 13.75, 21.30, 22.31, 25.64, 28.85, 31.42, 32.27, 33.09, 35.90 (Ar$\underline{C}H_3$, *n*-$\underline{C}_6H_{13}$, 3-$\underline{C}H_2$, 4-$\underline{C}H$), 51.55 ($\underline{C}H_3O$), 59.07 ($\underline{C}H_2S$), 126.98 (=$\underline{C}H_2$), 127.80, 129.54 (Ar), 136.85, 137.87 (Ar, =$\underline{C}$-CO_2Me), 144.16 (Ar), 166.93 ($\underline{C}$=O); *m/z* (NH_3, DCI) 384 (100%, MNH_4^+).

2-Methylene-5-(4-methylphenylsulfonyl)-4-phenylpentanoic acid, methyl ester (8cf). Prepared by the reaction of 2-[(4-methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7f**) with styrene (**6c**). The reaction was complete after 8h under reflux in carbon tetrachloride. 2-Methylene-5-(4-methylphenylsulfonyl)-4-phenylpentanoic acid, methyl ester (**8cf**) (58%) was obtained after flash chromatography using ethyl acetate / light petroleum (1:4 v/v) as the eluant; m.p.115.5-117.5°C (from ether / *n*-pentane); (Found: C, 67.0; H, 6.2. $C_{20}H_{22}O_4S$ requires: C, 67.3; H, 6.3%.); ν_{max} ($CHCl_3$) 1720, 1630, 1600, 1495, 1305, 1150cm^{-1}; δ_H(500MHz; $CDCl_3$) 2.40 (3H, s, Ar$C\underline{H}_3$), 2.61 (1H, dd, J=14, 7Hz, 3-C$\underline{H}$), 2.87 (1H, dd, J=14, 5Hz, 3-C$\underline{H}$), 3.47 (3H, m, 4-C$\underline{H}$ and 5-$C\underline{H}_2$), 3.68 (3H, s, $C\underline{H}_3O$), 5.37 (1H, t, J=7Hz, =C$\underline{H}$), 6.10 (1H, t, J=1Hz, =C$\underline{H}$), 6.97-7.18 (5H, m, Ph), 7.21 (2H, d, J=8Hz, Ar), 7.60 (2H, d, J=8Hz, Ar); δ_C(126MHz; $CDCl_3$) 21.5 (q, Ar$\underline{C}H_3$), 38.8 (t, C=C$\underline{C}H_2$), 39.8 (d, $\underline{C}$HPh), 51.8 (q, $\underline{C}H_3O$), 61.1 (t, $\underline{C}H_2SO_2$), 126.9 (d, Ar), 127.6 (d, Ar), 127.8 (t, C=$\underline{C}H_2$), 128.0 (d, Ar), 128.5 (d, Ar), 129.6 (d, Ar), 136.8 (s, Ar or $\underline{C}$=CH_2), 137.2 (s, Ar or $\underline{C}$=CH_2), 141.1 (s, Ar or $\underline{C}$=CH_2), 144.2 (s, Ar or $\underline{C}$=CH_2), 167.0 (s, $\underline{C}$=O); *m/z* (Probe CI, NH_3) 203 (100%), 359 (50%, MH^+), 376 (90%, MNH_4^+).

2-Methylene-4-(4-methylphenylsulfonyl)methyl-pentan-1,5-dioic acid, dimethyl ester (8df). Prepared by the reaction of 2-[(4-methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7f**) with methyl acrylate (**6d**). The reaction was complete after 8h under reflux in carbon tetrachloride. 2-Methylene-4-(4-methylphenylsulfonyl)methyl-pentan-1,5-dioic acid, dimethyl ester (**8df**) (69%) was obtained after flash chromatography using ether / *n*-pentane (1:1 v/v) as the eluant; m.p.110-112°C (from CH_2Cl_2 / *n*-pentane); ν_{max} ($CHCl_3$) 1735, 1630, 1600, 1440, 1315, 1150cm^{-1}; δ_H(500MHz; C_6D_6) 1.80 (3H, s, Ar$C\underline{H}_3$), 2.42 (2H, m, 3-$C\underline{H}_2$), 2.91 (1H, dd, J=14, 3Hz, C$\underline{H}SO_2$), 3.25 (3H, s, $C\underline{H}_3O$), 3.26 (3H, s, $C\underline{H}_3O$), 3.42 (1H, m, 4-C$\underline{H}$), 3.55 (1H, dd, J=14, 9Hz, C$\underline{H}SO_2$), 5.17 (1H, t, J=1Hz, =C$\underline{H}$), 6.04 (1H, s, =C$\underline{H}$), 6.69 (2H, d, J=8Hz, Ar), 7.73 (2H, d, J=8Hz, Ar); δ_C(126MHz; $CDCl_3$) 21.57 (q, Ar$\underline{C}H_3$), 34.76 (t, 3-$\underline{C}H_2$), 39.39 (d, 4-$\underline{C}$H), 51.99 (q, 2x$\underline{C}H_3O$), 56.97 (t, $\underline{C}H_2SO_2$), 128.28 (d, $\underline{C}H_2SO_2$), 129.50 (d, $\underline{C}H_2SO_2$), 136.20 (s, Ar), 144.87 (s, Ar), 166.44 (s, $\underline{C}$=O), 172.71 (s, $\underline{C}$=O); *m/z* (NH_3, Probe CI) 152 (100%), 341 (40%, MH^+), 384 (20%, MNH_4^+).

4-Cyano-2-methylene-5-(4-methylphenylsulfonyl)pentanoic acid, methyl ester (8ef). Prepared by the reaction of 2-[(4-methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7f**) with acrylonitrile (**6e**). Fresh benzoyl peroxide was added after 8h and the reaction was complete after 16h under reflux in carbon tetrachloride. 4-Cyano-2-methylene-5-(4-methylphenylsulfonyl)pentanoic acid, methyl ester (**8ef**) (42%) was obtained as an oil after flash chromatography using ether / *n*-pentane (1:1 v/v) as the eluant; ν_{max} ($CHCl_3$) 2250, 1720, 1635, 1600, 1445, 1330, 1150cm^{-1}; δ_H(500MHz; C_6D_6) 1.83 (3H, s, $ArC\underline{H}_3$), 2.11 (1H, dd, J=14, 9Hz, 3-C$\underline{H}$), 2.38 (1H, dd, J=14, 6Hz, 3-C$\underline{H}$), 2.64 (1H, dd, J=14, 5Hz, 5-C$\underline{H}$), 2.82 (1H, dd, J=14, 8Hz, 5-C$\underline{H}$), 3.24 (3H, s, $C\underline{H}_3O$), 3.33 (1H, m, 4-C$\underline{H}$), 5.24 (1H, s, =C$\underline{H}$), 6.09(1H, s, =C$\underline{H}$), 6.75 (2H, d, J=8Hz, Ar), 7.69 (2H, d, J=8Hz, Ar); *m/z* (NH_3, Probe CI) 325 (100%, MNH_4^+).

2-Methylene-5-(4-methylphenylsulfonyl)-4-phenylpent-4-enoic acid, methyl ester (24). 2-[(4-Methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7f**) with phenyl acetylene (**23**). The reaction was complete after 8h under reflux in carbon tetrachloride. Flash chromatography using ether / light petroleum (2:3 v/v) as the eluant allowed partial separation of 2-methylene-5-(4-methylphenylsulfonyl)-4-phenylpent-4-enoic acid, methyl ester (**24**) which was not separated completely from the starting sulfone (194mg; ratio **7f**:**24**=4:1 by ^{1}H n.m.r.; estimated yield of **24**: 70%). Further chromatography allowed separation of a pure sample of sulfone **24** (69mg; 25%) as a pale oil; (Found: C, 67.3; H, 5.75. $C_{20}H_{20}O_4S$ requires: C, 67.4; H, 5.65%.); δ_H(300MHz; $CDCl_3$) 2.37 (3H, s, $ArC\underline{H}_3$), 3.37 (2H, s, 3-$C\underline{H}_2$), 3.71 (3H, s, $C\underline{H}_3O$), 5.56 (1H, d, J=1Hz, =C$\underline{H}$), 6.30 (1H, s, =C$\underline{H}$), 6.50 (1H, s, =C$\underline{H}$), 7.05-7.38 (9H, complex, Ar and Ph).

Attempted Addition of 2-[(4-Methylphenylsulfonyl)methyl]propenoic acid methyl ester (7f) with Isopropenyl Acetate (14). After 16 h under reflux in carbon tetrachloride with fresh benzoyl peroxide having been added after 8h, the isopropenyl acetate had been consumed. Flash chromatography using ether / light petroleum (3:2 v/v) as the eluant allowed the isolation of the material gave 2-methylene-4,4-bis[(4-methylphenylsulfonyl)methyl]pentan-1,5-dioic acid, dimethyl ester (**16**) (8%); m.p. 151-154°C (from ether / *n*-pentane); (Found C, 57.0; H, 5.65. $C_{24}H_{28}S_2O_8$ requires: C, 56.65; H, 5.55%.); ν_{max}($CHCl_3$) 1735, 1600, 1495, 1320, 1150,cm^{-1}; δ_H(300MHz; $CDCl_3$) 2.47 (6H, s, 2x$ArC\underline{H}_3$), 3.22 (2H, s, 3-$C\underline{H}_2$), 3.63 (3H, s, $C\underline{H}_3O$), 3.72 (3H, s, $C\underline{H}_3O$), 4.01 (2H, d, J=14Hz, 2x$C\underline{H}SO_2$), 4.16 (1H, d, J=14Hz, 2x$C\underline{H}SO_2$), 5.79 (1H, s, =C$\underline{H}$), 6.32 (1H, s, =C$\underline{H}$), 7.38 (2H, d, J=8Hz, Ar), 7.89 (2H, d, J=8Hz, Ar); *m/z* (DCI NH_3) 526 (100%, MNH_4^+).

Reaction of Allylic Sulfones with Alkenes. Method B. A solution of the allylic sulfone (0.33mmol), the alkene (1.0mmol), and benzoyl peroxide (4mg, 17μmol, 5mol%) in ^{t}BuOH was heated under reflux until the reaction was complete (21-48h). The reaction mixture was diluted with ether, then washed with aqueous sodium hydroxide, water, and brine. The solution was then dried, filtered, and evaporated, and the product isolated by flash chromatography. The following sulfones were prepared by this method:

2-Methylene-3-[2-(4-methylphenylsulfonyl)cyclohex-1-yl]propanoic acid, methyl ester (18). Prepared by the reaction of 2-[(4-methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7f**) with cyclohexene (**17**). Flash chromatography using ethyl acetate / light petroleum (1:4 v/v) as the eluant gave 2-methylene-3-[2-(4-methylphenylsulfonyl)cyclohex-1-yl]propanoic acid, methyl ester (**18**) (36%); ν_{max} ($CHCl_3$) 2940, 1740, 1600, 1300, 1140cm^{-1}; δ_H(300MHz; $CDCl_3$) 1.03-2.04 (8H, m, 4x$C\underline{H}_2$), 2.05-2.20 (1H, m, CHCH$_2$C=C), 2.30 (1H, dd, J=15, 8Hz, 3-CH), 2.46 (3H, s, ArCH$_3$), 2.85 (1H, dt, J=8, 4Hz, CHSO$_2$), 3.20 (1H, dd, J=15, 4Hz, 3-CH), 3.72 (3H, s, OCH$_3$), 5.57 (1H, s, =CH), 6.20 (1H, s, =CH), 7.35 (2H, d, J=8Hz, Ar); *m/z* (NH$_3$, DCI) 337 (100%, MH$^+$).

2-Methylene-4-[(4-methylphenylsulfonyl)methyl]decanoic acid, methyl ester (8bf). Prepared by the reaction of 2-[(4-methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7f**) with 1-octene (**6b**). Flash chromatography using ethyl acetate / light petroleum (1:4 v/v) as the eluant gave 2-methylene-4-[(4-methylphenylsulfonyl)methyl]decanoic acid, methyl ester (**8bf**) (43%); data as quoted above.

2-Methylene-4-[(4-methylphenylsulfonyl)methyl]-N-phenyldecanamide (8bh). Prepared by the reaction of 2-[(4-methylphenylsulfonyl)methyl]propenoic acid methyl ester (**7h**) with 1-octene (**6b**). Flash chromatography using ethyl acetate / light petroleum (1:3 v/v) as the eluant gave 2-methylene-4-[(4-methylphenylsulfonyl)methyl]-N-phenyldecanamide (**8bh**) (66%) as a colourless oil; ν_{max} (CHCl$_3$) 3375, 2930, 1675, 1600, 1305, 1145cm^{-1}; δ_H(300MHz; CDCl$_3$) 0.85 (3H, s, CH$_3$), 1.03-1.53 (10H, m, 5-CH$_2$, 6-CH$_2$, 7-CH$_2$, 8-CH$_2$, 9-CH$_2$), 2.33-2.48 (1H, m, 4-CH), 2.40 (3H, s, ArCH$_3$), 2.52 (1H, dd, J=15, 8Hz, 3-CH), 2.77 (1H, dd, J=15, 6Hz, 3-CH), 3.07 (1H, dd, J=14, 6Hz, CHSO$_2$), 3.13 (1H, dd, J=14, 3Hz, CHSO$_2$), 5.43 (1H, s, =CH), 6.10 (1H, s, =CH), 7.13 (1H, t, J=7Hz, Ph), 7.23-7.42 (4H, m, Ar), 7.67-7.77 (4H, m, Ar); *m/z* (NH$_3$, DCI) 428 (100%, MH$^+$).

3-Methylene-5-(4-methylsulfonyl)tetrahydrofuran-2-one (28). Hydrated *p*-toluenesulfonic acid (0.6g) was dried by evaporation with toluene (50ml). Benzene (50ml), the sulfone (**8af**) (20mg, 59μmol) and methanol (0.5ml) were added, then the mixture was heated under reflux. After 6h, the solution was allowed to cool, then washed with saturated aqueous sodium bicarbonate, water, and brine, then dried (Na$_2$SO$_4$), filtered, and evaporated. Purification of the residue by flash chromatography using ether / light petroleum (3:1 v/v) as the eluant gave 3-methylene-5-(4-methylsulfonyl)tetrahydrofuran-2-one (**28**) (12mg, 45μmol, 76%); m.p. 95.5-96.5°C (from ether / *n*-pentane); (Found: C, 58.35; H, 5.4. C$_{13}$H$_{14}$O$_4$S requires: C, 58.6; H, 5.3%.); ν_{max} (CDCl$_3$) 1770, 1600, 1330, 1155cm^{-1}; δ_H(300MHz; CDCl$_3$) 2.48 (3H, s, ArCH$_3$), 2.97 (1H, m, 4-CH), 3.22-3.37 (2H, m, 4-CH and CHSO$_2$), 3.61 (1H, dd, J=14, 5Hz, CHSO$_2$), 4.92 (1H, m, 5-CH), 5.72 (1H, t, J=3Hz, =CH), 6.28 (1H, t, J=3Hz, =CH), 7.41 (2H, d, J=8Hz, Ar), 7.82 (2H, d, J=8Hz, Ar).

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