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The Effect of the Carbonyl Group in the Cyclization of 1-Hexenyl Radicals

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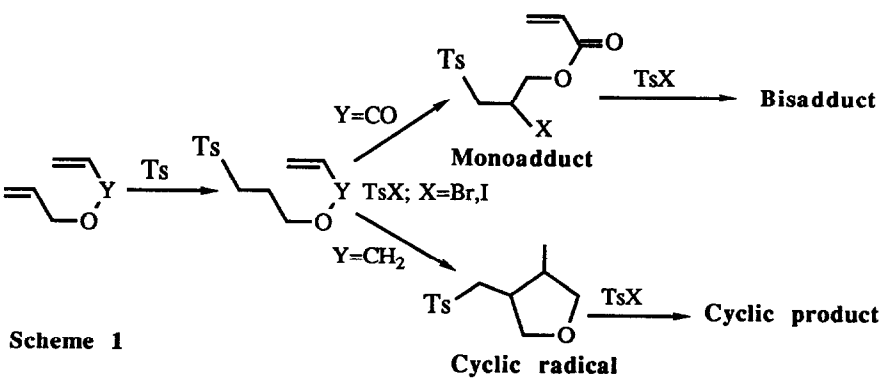
Abstract *- The radical chain cyclization of allyl ether derivatives promoted by tosyl halides and light is supressed by the presence of one carbonyl group conjugated with the double bond (acrylic double bond).*

INTRODUCTION

The radical chain cyclization of 1,6-dienes in the presence of sulphonyl halides has been successfully used to produce five and six membered rings with easily functionalized substituents (halogen atoms and sulphonyl groups) [1].

We report here the results of the light promoted additions of tosyl bromide (TsBr) and tosyl iodide (TsI) to 1,6-dienes (esters and ethers) in order to understand the effect of the the carbonyl group on the cyclization (Scheme 1). Studies of relative rates of addition of tosyl radicals to alkyl acrylates and alkyl allyl ethers have been carried out.

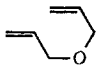
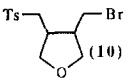
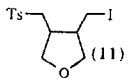
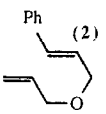
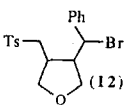
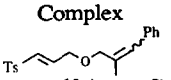
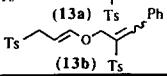
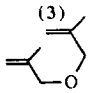
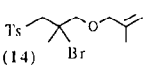
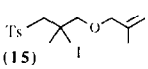


Scheme 1

RESULTS AND DISCUSSION

a)-The addition of tosyl halides to allylic ethers. Diallyl ether (**1**), in the presence of TsBr (or TsI) under visible light, yields the corresponding tetrahydrofurane derivatives, (**10**) and (**11**), in good yields. Tosyl iodide produces also the corresponding monoadduct and bisadduct [1b]. These results and those of other reactions with allyl ethers are summarized in Table 1.

Table 1- Results of the Light Promoted Addition of TsBr and TsI to Allylic Ethers, in Dichloromethane at Room Temperature.

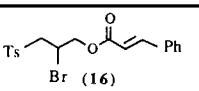
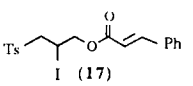
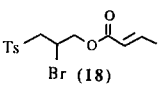
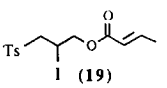
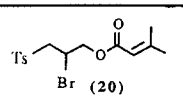
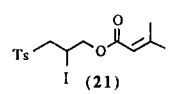
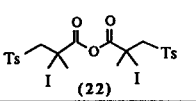
Diene	TsX	Reaction products	% Yield	[Diene] M	Ratio TsX/diene	Time
Diallyl ether (1) 	TsBr	 (10)	90 [a]	0.03	0.72	6 hr
			65 [a]	0.05	1.24	6 hr
	TsI	 (11)	51[b]	0.054	0.11	30 min
Allyl cinnamyl ether  (2)	TsBr	 (12)	47	0.52	1.30	24 hr
			30	0.17	1.30	24 hr
			20	0.09	1.30	24 hr
	TsI	Complex		0.01-0.03	0.50-1.20	30 min
		 (13a)  (13b)				
	TsI/TEA		25	0.07	3.90	30 min
Dimethallyl ether (3) 	TsBr	 (14)	43	0.08	0.60	24 hr
	TsI	 (15)	62	0.14	0.32	30 min

a) *cis/trans* =4/1 [1b]; b) *cis* isomer exclusively [1b]

Allyl cinnamyl ether (**2**), in the presence of TsBr, gave 20-47% of a mixture of diastereoisomers of the cyclic (**12**) (the *cis/trans* ratio of 4:1 was established after reduction with $NaBH_4$) resulting from the attack on the terminal double bond. No monoadduct was formed, showing that the cyclization is faster than the removal of bromine from TsBr. The attack on the non-terminal double bond only occured after the addition to the terminal double

bond. The addition of TsI yields a complex mixture of products; when used in excess (4:1) and treated with TEA, 25% of a mixture of isomeric dehydroiodated bisadduct (**13**) was obtained (with the tosyl radical located ß to the phenyl ring). The importance of the stereochemical and stabilization factors is evident in the lower yield of cyclization and slower reaction of allyl cinnamyl ether (**2**) as compared with diallyl ether (**1**). The lower reaction rate of (**2**) was confirmed by GLC; the results obtained showed that diallyl ether reacts approximately 5 times as fast as allyl cinnamyl ether. The delocalization of the unpaired electron over the aromatic ring in the cyclic radical may have a small accelerating effect on the

Table 2- Results of the Light Promoted Addition of TsBr and TsI to Allylic Esters, in Dichloromethane at Room Temperature.

Diene	TsX	Reaction products	% Yield	[Diene] M	Ratio TsX/diene	Time
Allyl cinnamate (4)	TsBr	 Br (16)	60-66	0.02-0.08	1.30	24 hr
	TsI	 I (17)	69[a]	0.13	3.40	20 min
			66	0.01	1.02	40 min
Allyl crotonate (5)	TsBr	 Br (18)	51	0.09	1.20	24 hr
			23	0.12	0.30	24 hr
	TsI	 I (19)	70	0.04	0.30	30 min
Allyl 3-methylcrotonate (6)	TsBr	 Br (20)	67	0.09	1.44	19 hr
			23[b]	0.02	1.20	60 hr
	TsI	 I (21)	65	0.09	1.91	30 min
Methacrylic anhydride (7)	TsBr	Polymer [c]		0.057	1.48	14 hr
		Polymer [c]		0.058	0.10	14 hr
	TsI	 (22)	40	0.14	2.90	40 min

a) No bisadduct was detected; b) 50% of ester was recovered; c) carbon tetrachloride as solvent.

cyclization step with early transition states,[2] but it may be these delocalization and steric effects that retard the propagation step (bromine abstraction) and slow down the overall reaction.

Dimethallyl ether (**3**) could not be cyclized either in the presence of TsBr or TsI, yielding the corresponding monoadducts, (**14**) and (**15**). The absence of cyclization seems to be the result of steric interactions between the tosyl and both methyl groups in the chair-like transition state [3].

b) The addition of tosyl halides to allylic esters. When the carbonyl group was introduced in the Y position (Scheme 1) no cyclic products could be obtained (Table 2).

Allyl cinnamate (**4**), allyl crotonate (**5**) and allyl 3-methylcrotonate (**6**) reacted only through the terminal double bond yielding the corresponding monoadducts. Contrasting with these results, several related compounds, such as ß-phenylselenocrotonates (and triphenyltin hydride) [4], allyl trichloroacetates (and cuprous salts) [5], and allylic esters of acetoacetic and malonic acids [and Mn(III)] [6] all lead to γ-lactone derivatives.

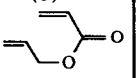
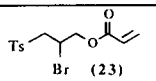
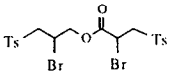
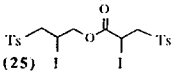
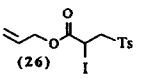
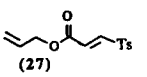
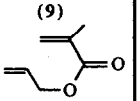
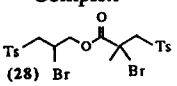
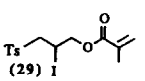
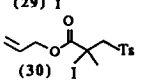
Methacrylic anhydride (**7**), in the presence of TsBr yielded a product that seems to be a polymer. When reacted with excess of TsI gave a bisadduct (**22**), since the propagation step of iodine removal is faster than the propagation step of the polymerization.

The results of the addition reactions to allyl acrylate (**8**) and allyl methacrylate (**9**), with two terminal double bonds, are summarized in Table 3.

Allyl acrylate (**8**) in the presence of TsBr, gave the the bisadduct (**24**) and another product that seems by RMN ^{1}H, ^{13}C to be the monoadduct (**23**). With TsI (**8**) gave 35% of the bisadduct (**25**) and 32% of the monoadduct (**26**) resulting from the attack of Ts· on the acrylic double bond; with excess of TsI the bisadduct (**25**) was obtained. With excess of olefin (3:1) the unsaturated sulphone (**27**) was again obtained, confirming that the attack on the acrylic double bond is preferred. Although the delocalization of the unpaired electron over the carbonyl group is important in reactions with late transition states [7], this was unexpected here since, in reactions with early transition states, the carbonyl group should decrease the rate of addition of electrophilic species, such as arenesulphonyl radicals [8,9], due to polar effects.

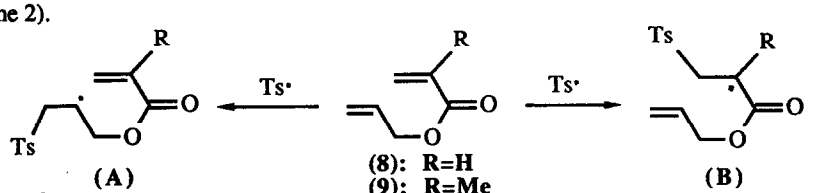
Allyl methacrylate (**9**) in the presence of TsBr gave a complex mixture of products; a large excess of TsBr yielded the bisadduct (**28**) in low yield. With TsI two monoadducts were obtained, (**29**) and (**30**), resulting from the attack on the allylic and acrylic double bond, respectively.

Table 3- Results of the Light Promoted Addition of TsBr and TsI to Allyl Acrylate and Allyl Methacrylate , in Dichloromethane at Room Temperature.

Diene	TsX	Reaction products	% Yield	[Diene] M	Ratio TsX/diene	Time
Allyl acrylate (8) 	TsBr	 (23)	11	0.02	4.2	24 hr
		 (24)	19			
	TsI	 (25)	66	0.1	3.1	40 min
		 (26)	32 [a]	0.08	1.2	30 min
		(25)	35			
	TsI/TEA	 (27)	44	0.10	0.34	30 min
			31	0.03	0.60	30 min
Allyl methacrylate (9) 	TsBr	Complex		0.09	1.16	24 hr
		 (28)	16	0.017	5.13	24 hr
	TsI	 (29)	16	0.21	0.33	30 min
		 (30)	37			

a) isolated as dehydroiodated product (27)

The results summarised in Tables 1,2 and 3 confirm that tosyl radicals attack the terminal double bonds preferentially but the most important conclusion concerns the lack of cyclization in the presence of a carbonyl group conjugated with the double bond or with the radical centre (Scheme 2).



Scheme 2

Studies with models show that, in the radical (**A**) (Figure 1) obtained from the addition of Ts· to the terminal double bond, the 1-5 and 1-6 distances for convenient p-π^* interaction [10] are considerably bigger in the case of planar systems than in non-planar ones (Figure 1).

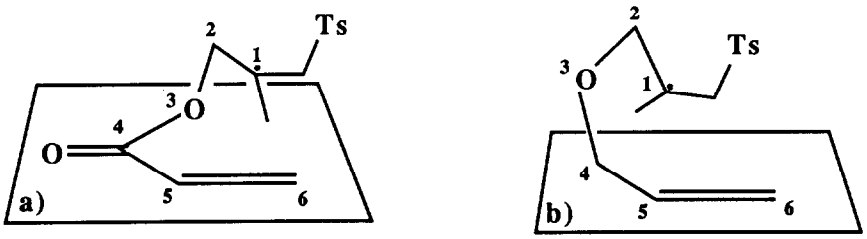


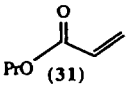
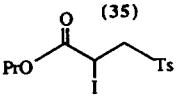
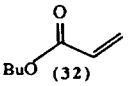
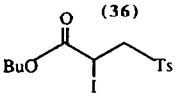
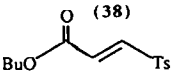
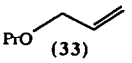
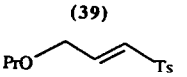
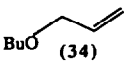
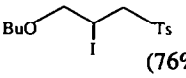
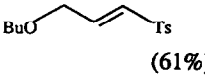
Figure 1-Planar and non-planar transition states for cyclization of 5-hexenyl radicals: a)Y=CO and b)Y=CH_2.

The requirement of the unfavorable ester *cis* conformation for cyclization is another reason for slowing down the reaction[11]. In these cases (as compared with reported examples [4]) cyclization is too slow to compete with the fast propagation steps of iodine or bromine abstraction from the tosyl halide.

Cyclization of radical (**B**) (Scheme 2) is also slowed down since the geometry of the transition state is also severely restricted due to the overlap between the radical centre and the carbonyl group . This stereoelectronic effect is the reason for the significant reversal in regioselectivity in compounds with carbonyl substitution inside the forming ring [12] .In the reactions of dienes (**7**) the internal addition to the double bond was slower than the abstraction of iodine, but different behaviour is found in the case of TsBr, where the addition of the radical (**B**) to the acrylic double bond of another molecule (electron deficient olefin), is faster than the internal addition or even the bromine abstraction, and we obtain polymerization.

c)-Relative reactivities of addition. In order to understand the behaviour observed in the addition of TsI and TsBr to allyl methacrylate (**7**) and allyl acrylate (**8**), namely the greater extent of the addition to the acrylic double bond, we carried out a study of the relative reactivities of addition of tosyl radicals to allylic and acrylic double bonds. The addition of tosyl iodide to propyl acrylate (**31**), butyl acrylate (**32**), allyl propyl ether (**33**), and allyl butyl ether (**34**) in dichloromethane solution, under visible light, yielded the corresponding adducts, (**35**) to (**40**), in good yield (Table 4).

Table 4-Results of the Light Promoted Addition of TsI to Alkyl Acrylates and Alkyl Allyl Ethers, in Dichloromethane, at Room Temperature, for 30 Minutes (Molar Ratio1:1).

Olefin	Reaction product (yield%)	Dehydroiodated product (yield%)
Propyl acrylate  (31)	 (35) (97%)	
Butyl acrylate  (32)	 (36) (93%)	 (38) (88%)
Allyl propyl ether  (33)		 (39) (64%)
Allyl butyl ether  (34)	 (37) (76%)	 (40) (61%)

The adducts, which decomposed easily on standing, were treated with triethylamine (TEA) to yield the corresponding unsaturated sulphones **(38)** to **(40)**.

Relative reactivities of the double bonds towards tosyl radicals were measured by competition experiments based on reactions (1) and (2), by using the equation (3) where $[M_1]_o$, $[M_2]_o$ and $[M_1]$, $[M_2]$ are the initial and final concentrations of both olefins in competition.

$$Ts^{\bullet} + \begin{cases} M_1 \xrightarrow{k_1} \text{Radical adduct 1} & (1) \\ M_2 \xrightarrow{k_2} \text{Radical adduct 2} & (2) \end{cases}$$

$$k_1/k_2 = (\log[M_1] - \log[M_1]_o)/(\log[M_2] - \log[M_2]_o) \qquad (3)$$

These concentrations were determined by GLC; the same technique was also applied to the determination of relative reactivities of the reactions of arenesulphonyl radicals with styrenes [8] and to substituted acetylenes [9].

Table 5 summarizes the results of the competition experiments and shows that the allylic double bond is as reactive as the acrylic double bond; the conjugated carbonyl group has no effect on the reactivity of the olefins towards tosyl radicals.

Table 5-Relative Rates of Addition of Ts· to Alkyl Acrylates and Alkyl Allyl Ethers, in Dichloromethane, at 30.5°C.

Olefin 1	Olefin 2	k_1/k_2 (stand. dev.)	Number of runs
Propyl acrylate (**31**)	Allyl propyl ether (**33**)	1.01 (0.05)	12
Butyl acrylate (**32**)	Allyl butyl ether (**34**)	1.04 (0.06)	11
Propyl acrylate (**31**)	Butyl acrylate (**32**)	0.99 (0.06)	9

This may be rationalized by the participation of two opposing and compensating effects of the carbonyl group: the first one concerns the decrease of rate due to polar effects in the transition state (Figure 2) and the second one the acceleration due to the delocalization of the unpaired electron of the incipient radical over the carbonyl, despite the early transition state of the addition. A similar stabilization (much more pronounced) with electrophilic radicals was found in the addition of *t*-butoxy radicals to allyl methacrylate where the reaction is believed to take place through a late transition state; the relative reactivity of the two types of bonds is acrylic/allylic=203/19 (tail addition) [13].

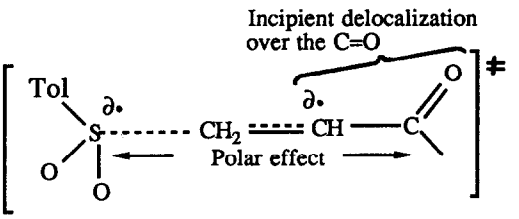


Figure 2- Polar and resonance effects in the transition state of the addition of Ts to acrylate esters.

When both types of terminal bonds (acrylic and alllylic) are present in the same molecule, as in the cases of allyl acrylate (**8**) and allyl methacrylate (**9**), the adduct resulting from the addition of TsI to the acrylic double bond is formed in greater extent. This can be seen through the results presented in Table 3, which were confirmed by the HPLC analysis of the reaction mixtures. The reason is believed to be the greater stability of the radical conjugated with the double bond (in Scheme 2) [the delocalization energy of a radical of the type **B** is about 23 kcal/mol [14] and the delocalization energy of a double bond conjugated with a carbonyl group (type **A**) is only about 4 kcal/mol [15]]. Since the addition of tosyl radicals to olefins is a reversible process[16], radical (**A**) in Fig 3 may isomerize into the more stable radical (**B**) which would yield the corresponding monoadduct. This effect is less important in the addition to allyl methacrylate (R=Me), since the propagation step for iodine removal by the adduct radical is slower in the presence of an α-methyl substituent in the adduct radical. A similar steric effect of the α-methyl group was seen in the addition of arenesulphonyl iodides to α-methyl styrene where no addition product was formed (an α,β-unsaturated sulphone was obtained)[17].

Figure 3 summarizes the participation of the polar, resonance and steric effects in the addition and propagation steps of the reaction.

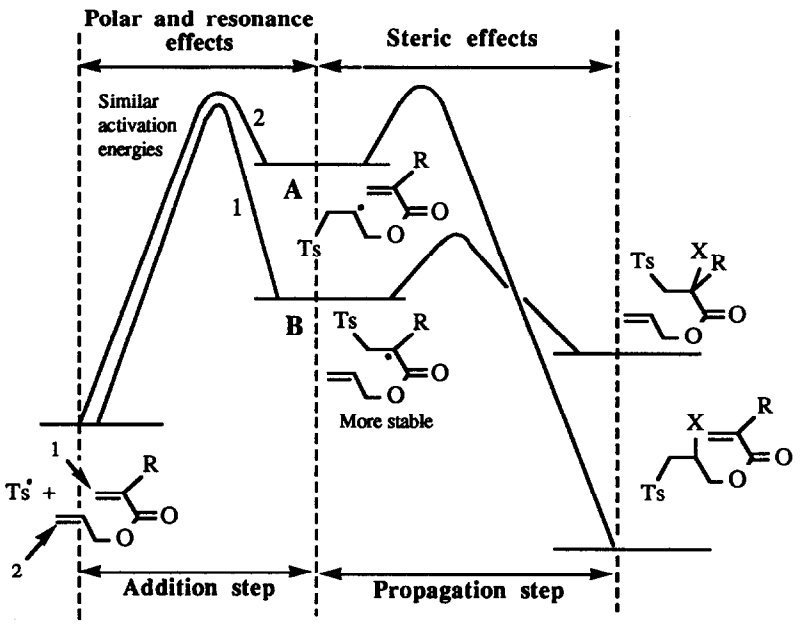


Figure 3- Polar, resonance, and steric effects on the addition and propagation steps of the reaction of TsI with allyl acrylate (R=H) and allyl methacrylate (R=Me) .

EXPERIMENTAL

Tosyl iodide[18] and bromide[19] were prepared from sodium *p*-toluenesulphinate. Allyl methacrylate (Aldrich), methacrylic anhydride (Aldrich), allyl propyl ether (Aldrich), allyl butyl ether (Aldrich), other chemicals and solvents (good grade commercial products) were used without further purification. IR and NMR spectra were recorded on a Philips PU 9800 spectrophotometer and Bruker AC-200 spectrometer, respectively. When it seemed necessary resonance multiplicities for ^{13}C were established *via* DEPT sequence. Distillation was carried out on a microdestillation apparatus.Melting points for solid products were determined using a digital Electrothermal apparatus, and are uncorrected. Preparative chromatography was carried out on columns using Merck Kieselgel 60, 70-230 mesh, Art.º 7754. For separation of reaction products in cromatothron plates of Merck Kieselgel 60 Pf_{254} Art.º 7759 were used. Irradiation of solutions was made under visible light using a Philips HP/T 200W lamp, during the specified time.

Allyl cinnamyl ether (2)[20]. A mixture of 10.0 g (74.5 mmol) of cinnamyl alcohol, 6.80 g (117 mmol) of allyl alcohol, 0.40 g (1.26 mmol) of mercuric acetate and 0.15 g (0.99 mmol) of boron trifluoride etherate (recently distilled) in benzene (6 mL) was heated under reflux with a Dean-Stark separator. After 2 hours, the reaction mixture was diluted with diethylether (20 mL), washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure (room temperature) and the residue purified by distillation (0.1 g of hydroquinone was added to avoid polymerization) at 1 mm Hg to give 6.8 g (55%) of (2) as a colourless oil. IR (liquid film) 3070, 3060, 3020, 2900, 2850, 1605, 1500, 1440, 1120, 1070, 950, 740, 710 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.40-7.12 (m, 5H, Ph), 6.54 (d, 1H, J=15.9 Hz, CH=CHBr), 6.15 (dt, 1H, J=15.9, 5.8 Hz, CH=CHPh), 6.28-6.17 (m, 1H, $CH=CH_2$), 5.31-5.11 (m, 2H, CH_2=), 4.06 (dd, 2H, J=5.8, 1.3 Hz, O-CH_2-CHCHPh), 3.95 (dt, 2H, J=5.5, 1.5, Hz, O-CH_2-$CHCH_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 136.42 (Ph), 134.53 (CH_2=CH), 131.90 (PhCH), 128.20 (Ph), 127.27 (CH=CHPh), 126.15 (Ph), 125.76 (Ph), 116.47 (CH_2=), 70.65 (O-CH_2), 70.27 (O-CH_2).

Dimethallyl ether (3) A mixture of 8.60 g (110 mmol) of methallyl alcohol, 2.70 g (120 mmol) of sodium in THF (15 mL) was refluxed overnight. After this period 11.0 g (122 mmol) of methallyl chloride were added and the mixture refluxed for a further 8 hours, with stirring. The mixture was poured into water (100 mL) and extracted with diethylether. The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. The oily residue was distilled (0.1 g of hydroquinone was added to avoid polymerization) at 10 mm Hg to give 8.25 g (55%) of (3) as a colourless oil. IR (liquid film) 3060, 2990, 2900, 2875, 1650, 1450, 1105, 1090, 900 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 4.89-4.98 (m, 4H, CH_2=), 3.86 (s, 4H, O-CH_2), 1.74 (s, 6H, Me). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 142.27 (MeC=), 111.91 (CH_2=), 73.77 (O-CH_2), 19.44 (Me).

Allyl cinnamate (4). A solution of 10.0 g (60.0 mmol) of cinamoyl chloride in ethyl ether (10 mL) was added dropwise with stirring to a solution of 8.60 g (148 mmol) of allyl alcohol, 5.1 mL (63 mmol) of pyridine in ethyl ether (40 mL). The reaction mixture was left under stirring at room temperature for 4 hours, washed with Na_2CO_3 (10%), water and dried ($CaCl_2$). The solvent was removed under reduced pressure and the liquid obtained was distilled at P=0.4 mmHg (0.1 g of hidroquinone was added to avoid polymerization) to give 8.1 g (72%) of (4) as a colourless liquid. IR (liquid film): 1713, 1637, 1450, 1309, 1203, 1169, 1018, 989, 979, 767, 711, 684 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.68 (d, 1H, J=16.0 Hz, Ph-CH=), 7.31-7.48 (m, 5H, Ph), 6.43 (d, 1H, J=16.0 Hz, =CH-CO), 5.90-6.04 (m, 1H, CH=CH_2), 5.22-5.40 (m, 2H, =CH_2), 4.68 (d, 2H, J=4.5 Hz, CH_2-O). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 186.13 (CO), 144.78 (Ph-CH=), 134.26 (CH=CH_2), 132.25 (Ar), 130.10 (Ar), 128.70 (Ar), 127.93 (Ar), 117.99 (=CH_2), 117.79 (=CH-CO), 64.92 (CH_2-O).

Allyl crotonate (5). A mixture of 10.0 g (64.9 mmol) of crotonic anhydride, 15.0 g (258 mmol) of allyl alcohol and 1mL of conc. sulfuric acid in THF (10 mL) was refluxed for 2 hours, cooled, diluted with CH_2Cl_2 (50 mL), washed with water, Na_2CO_3 (10%) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the remaining liquid was distilled (P=15 mmHg) to give 4.5g (55%) of (5) as a colourless liquid. IR (liquid film): 1720, 1660, 1444, 1379, 1361, 1311, 1294, 1259, 1178, 1103, 1024, 993, 970, 931, 839 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.90-7.11 (dq, 1H, J=15.5, 6.9 Hz, =CH-CO), 5.82-6.06 (m, 2H, Me-CH=, =CH-CH_2-O), 5.19-5.43 (m, 2H, =CH_2), 4.62 (dt, 2H, J=5.6, 1.3 Hz, CH_2-O), 1.89 (dd, 3H, J=6.9, 1.7 Hz, Me). ^{13}C NMR ($CDCl_3$, 200 MHz): 166.09 (CO), 144.92 (Me-CH=), 132.32 (CH=), 122.41(=CH-CO), 117.90 (=CH_2), 64.76 (CH_2-O), 17.91 (Me).

Allyl 3-methylcrotonate (6). A mixture of 9.0 g (90 mmol) of 3,3-dimethylacrylic acid, 15.4 g (265 mmol) of allyl alcohol and 1 mL of conc. sulfuric acid was refluxed for 2 hours, cooled, diluted with CH_2Cl_2 (50 mL), washed with water, Na_2CO_3 (10%) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the remaining liquid was distilled (P=10 mmHg) to give 5.5g (44%) of (6) as a colourless liquid. IR (liquid film): 1720, 1649, 1446, 1379, 1273, 1226, 1145, 1076, 993, 931 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 5.87-6.10 (m, 1H, CH=CH_2), 5.71 (hep., 1H, J=1.3 Hz, =CH-CO), 5.18-5.36 (m, 2H, =CH_2), 4.59 (dt, 2H, J=5.6, 1.4 Hz, CH_2-O), 2.18 (d, 3H, J=1.3 Hz, *(Z)* Me-C=C, 1.90 (d, 3H, J=1.3 Hz, *(E)* Me-C=C . ^{13}C NMR ($CDCl_3$, 200 MHz): δ 166.00 (CO), 156.90 (Me_2C=), 132.55 (CH=), 117.53 (=CH_2), 115.63 (=CH-CO), 64.06 (CH_2-O), 27.22 (*(Z)* Me-C=C), 20.03 (*(E)* Me-C=C) .

Allyl acrylate (**8**). A solution of 5.6 g (62 mmol) of acryloyl chloride in ethyl ether (5 mL) was added dropwise (caution: vigorous reaction) to a solution of 3.0 g (52 mmol) of allyl alcohol, 8.4 g (83 mmol) of triethylamine in ethyl ether (50 mL) at 0°C. After sitirring for 4 hours at room temperature, the mixture was poured into water (100 mL) and extracted with ethyl ether. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated in vacuo. The remaining liquid was distilled (P=10 mmHg, 0.1 g of hidroquinone is added to avoid polymerization) to give 3.2 g (60%) of (**8**) as a colourless liquid. IR (liquid film): 1728, 1651, 1635, 1620, 1406, 1296, 1273, 1188, 1053, 985, 933, 810 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.45 (dd, 1H, J=17.2, 1.7 Hz, *(Z)* CH=CH-CO) , 6.10-6.25 (dd, 1H, J=17.2, 10.3 Hz, =CH-CO), 5.91-6.05 (m, 1H, =CH-CH_2-O), 5.85 (dd, 1H, J=10.3, 1.7 Hz, *(E)* CH=CH-CO), 5.22-5.40 (m, 2H, =CH_2), 4.64-4.68 (dt, 2H, J=5.7, 1.3 Hz, CH_2-O). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 165.77 (CO), 132.04 (CH=), 130.85 (=CH_2), 128.26 (=CH-CO), 118.22 (=CH_2 allylic), 65.11 (CH_2-O).

3-(Bromophenylmethyl)-4-*p*-toluenesulphonylmethyltetrahydrofuran (**12**) (mixture of diasteroisomers). A solution of 0.87 g (3.70 mmol) of tosyl bromide, 0.50 g (2.9 mmol) of allyl cinnamyl ether in dichloromethane (5.5 mL) was irradiated at room temperature for 24 hours. The solvent was removed under reduced pressure and the remaining oil was purified in a Chromatotron, model 7924T (Harrison Research) (CH_2Cl_2 /AcOEt -95:5) to give an oil that when treated with a few mL of carbon tetrachloride gave 0.56 g (47%) of (**12**) as a white solid , m.p. 111-115°C (CCl_4). Anal. Calc. for $C_{19}H_{21}O_3SBr$: C, 55.8; H, 5.1; O, 11.7; S, 7.8; Br, 19.5; Found: C, 55.2; H, 5.1; O, 11.6; S, 9.7; Br, 18.4. IR (Nujol): 1590, 1311, 1302, 1292, 1167, 1136, 1086, 1049, 904, 846, 815, 711, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.19-7.98 (m, 9H, Ph, Ar), 4.87-2.81 (m, complex, 9H, CH_2Tos, CH_2-O, CH, CHBr), 2.41-2.46 (s, 3H, Me-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 144.92 (Ar, *cis/trans*), 144.51 (Ar, *cis*), 139.81 (Ph, *trans*), 139.53 (Ph, *cis*), 136.21 (Ar, *cis/trans*), 135.54 (Ar, *cis/trans*), 129.86 (Ar, *cis/trans*), 129.18 (Ph, *cis/trans*), 128.21 (Ph, *cis/trans*), 127.53 (Ar, *cis/trans*), 126.98 (Ph,*cis/trans*), 72.60 (CH_2-O, *cis*), 72.22 (CH_2-O, *cis*),71.78 (CH_2-O, *trans*), 69.09 (CH_2-O, *trans*), 53.04 (CH_2Tos, *trans*), 52.81 (CH_2Tos, *cis*), 51.97 (CH-CHBr, *cis*), 51.71 (CH-CHBr, *trans*), 51.30 (CH-Br, *trans*), 49.11 (CH-Br, *trans*), 21.53 (Me-Tos, *cis/trans*).

Reduction of (**12**). *(cis/trans)* 3-Phenylmethyl-4-*p*-toluenesulphonylmethyltetrahydrofuran. To a solution of 0.30 g (0.73 mmol) of cyclic compound (**12**) in THF (5 mL) was added a solution of 0.17 g (4.50 mmol) of sodium tetraborohydride in DMSO (3 mL), and the mixture refluxed for 4 hours. The reaction mixture was poured into a solution of 25 mL of HCl (10%) and 25 mL of water, extracted with CH_2Cl_2 (75 mL), washed with Na_2CO_3 (10%), water and dried ($MgSO_4$). The solvent was removed under reduced pressure and the remaining residue was chromatographed (CH_2Cl_2) and gave 0.15 g (62%) of *(cis/trans)* 3-phenylmethyl-4-*p*-toluenesulphonylmethyltetrahydrofuran as a colourless oil (identified as a

mixture of the *cis/trans* isomers, 4:1). Anal. Calc. for $C_{19}H_{22}O_3S$: C, 69.1; H, 6.7; O, 14.5; S, 9.7; Found: C, 68.6; H, 6.8; O, 14.6; S, 9.7. IR (liquid film) 3071, 3052, 2925, 2810, 1602, 1494, 1440, 1312, 1309, 1128, 1096, 1066, 812 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.07-7.79 (m, 9H, Ph, Ar), 2.50-4.11 (m, 10H, $\underline{CH_2}$Tos, $\underline{CH_2}$Ph CH_2-O, CH), 2.45 (s, 3H, $\underline{Me}$-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz) *cis* isomer: δ 144.88 (Ar), 139.31 (Ar), 136.40 (Ar), 130.09 (Ar), 128.60, (Ph), 128.50 (Ph), 127.89 (Ar), 126.26 (Ph), 71.43 (CH_2-O), 71.31 (CH_2-O), 54.97 (CH_2Tos), 43.05 ($\underline{CH}$-CH_2Ph), 36.55 ($\underline{CH}$-CH_2Tos), 33.88 (CH_2Ph), 21.53 ($\underline{Me}$-Ar); *trans* isomer: 144.88 (Ar), 139.15 (Ph), 136.15 (Ar), 128.60 (Ph), 128.50 (Ph), 127.89 (Ar), 126.26 (Ph), 72.81 (CH_2-O), 72.33 (CH_2-O), 59.40 (CH_2Tos), 46.58 ($\underline{CH}$-CH_2Ph), 39.45 ($\underline{CH}$-CH_2Tos), 38.54 ($\underline{CH_2}$Tos), 21.53 ($\underline{Me}$-Ar).

1-(3-*p*-Toluenesulphonyl-2-propenoxy)-2-*p*-toluenesulphonyl-3-phenyl-2-propene (**13a**) and 1-(3-*p*-Toluenesulphonyl-1-propenoxy)-2-*p*-toluenesulphonyl-3-phenyl-2-propene (**13b**). A solution of 1.9 g (6.7 mmol) of tosyl iodide and 0.30 g (1.7 mmol) of allyl cinnamyl ether in dichloromethane (25 mL) was irradiated for 30 min.. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water, and dried ($CaCl_2$) and the solvent was removed under reduced pressure. To the oily residue ethyl acetate (5 mL) were added, and 1mL of triethylamine dropwise. The ammonium salt precipitated immediately; the solution was stirred for 2 hours at 50 °C. After filtration it was diluted with ethyl ether (30 mL), washed with water, dilute solution of HCl and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product purified by column chromatography (petroleum ether 40-60°C / AcOEt -2:1) to give as a 2nd fraction 0.25 g (25%) of (**13a** and **13b**) as an oil. IR (liquid film) 3066, 2954, 2946, 1665, 1648, 1600, 1314, 1304, 1154, 1141, 1115, 1098, 1087, 1037,920, 818, 743, 737 cm^{-1}

13a ^1H NMR ($CDCl_3$, 200 MHz): δ 8.03 (s, 1H, Ph$\underline{CH}$=), 7.86-7.21 (m, complex, 13H, Ph, Ar), 6.77 (d broad, 1H, J=15.0 Hz, Tos$\underline{CH}$=), 6.24 (d broad, 1H, J=15.0 Hz, TosCH=$\underline{CH}$), 4.35-4.05 (m, 4H, CH_2-O), 2.44 (s, 3H, $\underline{Me}$-Ar), 2.29 (s, 3H, $\underline{Me}$-Ar).

13b ^1H NMR ($CDCl_3$, 200 MHz): δ 8.03 (s, 1H, Ph$\underline{CH}$=), 7.86-7.21 (m, complex, 13H, Ph, Ar), 6.10 (d, 1H, J=6.1 Hz, =CH-O), 4.50-4.35 (m, 3H, CH_2-O, Tos$CH_2\underline{CH}$=), 3.47 (d, 2H, J=7.9 Hz, CH_2Tos), 2.44 (s, 3H, $\underline{Me}$-Ar), 2.26 (s, 3H, $\underline{Me}$-Ar).

13a ,13b ^{13}C NMR ($CDCl_3$, 200 MHz) δ 149.33 (=CH-O), 144.70(Ar), 144.48 (Ar), 144.29 (Ar), 144.25, (Ar), 144.19 (=CH-Tos), 144.18 (=CH-Tos), 137.28 (Ar), 137.00 (Ar), 136.88 (Ph), 136.50 (Ar), 135.68 (Ar), 132.39 (=CHPh), 132.25 (=CHPh), 130.57 (Ph), 130.36 (Ph), 130.17 (Ar), 129.84 (Ar), 129.76 (Ar), 129.66 (Ar), 129.30 (Ph), 128.88 (Ph), 128.86 (Ph), 128.22 (Ar9, 128.21 (Ar),128.14 (Ar), 128.05 (Ar), 93.9 (Tos$CH_2\underline{CH}$=), 91.45 ($CH_2\underline{CH}$=CH), 67.73 (O$\underline{CH_2}$CH=), 64.03 (O$\underline{CH_2}$CTos), 65.54 (O$\underline{CH_2}$CTos), 52.10 ($\underline{CH_2}$-Tos), 21.48 ($\underline{Me}$-Ar), 21.37 ($\underline{Me}$-Ar)

2-Bromo-2-methyl-1-(2-methyl-2-propenoxy)-3-*p*-toluenesulphonylpropane (**14**). A solution of 0.32 g (1.4 mmol) of tosyl bromide and 0.52 g (4.1 mmol) of dimethallyl ether in dichloromethane (50 mL) was irradiated for 24 hours. The solvent was removed under reduced pressure and the remaining oil was chromatographed (CH_2Cl_2/AcOEt 95:5) to give 0.21 g (43%) of (**14**) as a colourless oil. IR (liquid film) 2978, 2928, 2863, 1660, 1597, 1451, 1402, 1381, 1321, 1304, 1291, 1150, 1087, 902, 839, 818, 736, 679 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.78 (d, 2H, J=8.3 Hz, Ar), 7.34 (d, 2H, J=8.0 Hz, Ar), 4.97 (s, 1H, $=CH_2$), 4.90 (s, 1H, $=CH_2$) 3.60-4.11 (m, 6H, CH_2-O, CH_2-Tos), 2.43 (s, 3H, Me-Ar), 2.06 (s, 3H, Me-CHBr), 1.75 (s, 3H, Me-C=). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 144.67 (Ar), 141.42 (Me-C=), 137.60 (Ar), 129.70 (Ar), 127.62 (Ar), 112.36 ($=CH_2$), 76.47 (O-CH_2-CHBr), 74.89 (O-CH_2-C=), 64.29 (CH_2-Tos), 60.46 (CBr), 28.11 (Me-CBr), 21.40 (Me-Ar), 19.22 (Me-C=).

2-Iodo-2-methyl-1-(2-methyl-2-propenoxy)-3-*p*-toluenesulphonylpropane (**15**). A solution of 0.37 g (1.3 mmol) of tosyl iodide and 0.52 g (4.1 mmol) of dimethallyl ether in dichloromethane (30 mL) was irradiated for 30 minutes. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water, and dried ($CaCl_2$).The solvent was removed under reduced pressure and the remaining oil was purified in a Chromatotron, model 7924T (Harrison Research) (CH_2Cl_2) to give 0.33 g (62%) of (**15**) as an oil. IR (liquid film) 2976, 2926, 1661, 1597, 1448, 1400, 1381, 1319, 1304, 1290, 1149, 1120, 1086, 903, 817, 731, 675 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.77 (d, 2H, J=8.3 Hz), 7.34 (d, 2H, J=8.5 Hz), 4.98 (s,1 H, $=CH_2$), 4.92 (s, 1H, $=CH_2$), 4.15 (d, 1H, J=14.0 Hz, CH-Tos), 3.96 (s, 2H, O-CH_2-C=), 3.80 (d, 1H, J=14.0 Hz, CH-Tos), 3.63 (s, 2H, O-CH_2-CI), 2.43 (s,3H, Me-Ar), 2.31 (s, 3H, Me-CHI), 1.77 (s, 3H, Me-C=). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 144.66 (Ar), 141.51 (Me-C=), 137.70 (Ar), 129.74 (Ar), 127.55 (Ar),112.38 ($=CH_2$), 78.42 (O-CH_2-CI), 74.75 (O-CH_2-C=), 67.09 (CH_2-Tos), 41.80 (CI), 30.98 (Me-CHI), 21.44 (Me-Ar), 19.42 (Me-C=).

2-Bromo-3-*p*-toluenesulphonylpropyl cinnamate (**16**). A solution of 1.6 g (6.8 mmol) of tosyl bromide and 1.0 g (5.35 mmol) of allyl cinnamate in dichloromethane (100 mL) was irradiated for 24 hours. The solvent was removed under reduced pressure and the remaining oil was treated with methanol and left in the refrigerator to give 1.49 g (66%) of (**16**) as a white solid, m.p. 93-94.5 °C (MeOH). Anal. Calc. for $C_{19}H_{19}O_4SBr$: C, 53.9; H, 4.49; Found: C, 53.2; H, 4.49. IR (Nujol) 1707, 1635, 1313, 1304, 1182, 1143, 991, 765, 756, 535, 520 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.70 (d, 1H, J=16.0 Hz, Ph-CH=), 7.25-7.90 (m, 9H, Ph, Ar), 6.42 (d, 1H, J=16.0 Hz, CH-CO), 4.56 (m broad, 3H, CHBr, O-CH_2), 4.85-3.56 (m, 2H, CH_2-Tos), 2.43 (s, 3H, Me-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 165.80 (CO), 146.01 (HC=CPh), 145.42 (Ar), 135.90 (Ar), 133.97 (Ph), 130.08 (Ar), 128.86 (Ar), 128.13 (Ph), 116.71 (HC=CO), 66.15 (O-CH_2), 60.55 (CH_2-Tos), 39.67 (CHBr), 21.59 (Me-Ar).

2-Iodo-3-*p*-toluenesulphonylpropyl cinnamate (**17**). A solution of 0.92 g (3.3 mmol) of tosyl iodide and 0.60 g (3.21 mmol) of allyl cinnamate in dichloromethane (250 mL) was irradiated for 40 minutes. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water and dried ($CaCl_2$).The solvent was removed under reduced pressure and the remaining oil was treated with ethanol and left in the refrigerator overnight to precipitate 1.0 g (66%) of (**17**) as a white solid, m.p.= 94.5-95.5 °C (MeOH/EtOH -2:1). Anal.Calc for $C_{19}H_{19}O_4SI$: C, 48.5; H, 4.0; Found: C,48.0; H, 4.0. IR (Nujol) 1708, 1645, 1312, 1280, 1251, 1179, 1146,. 990, 809, 755, 743, 519 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.62 (d, 1H, J=16 Hz, Ph-CH=), 7.31-7.88 (m, 9H, Ph), 6.41 (d, 1H, J=16 Hz, CH-CO), 4.45-4.68 (m, 3H, O-CH_2, CHI), 3.64-3.96 (m, 2H, CH_2-Tos), 2.43 (s, 3H, Me-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 165.75 (CO), 145.97 (HC=CPh), 145.46 (Ar), 135.98 (Ar), 134.00 (Ph), 130.58 (Ph), 130.19 (Ar), 129.18 (Ph), 128.92 (Ar), 116.97 (HC=CO), 67.56 (O-CH_2), 62.44 (CH_2-Tos), 21.64 (Me-Ar), 13.98 (CHI).

2-Bromo-3-*p*-toluenesulphonylpropyl crotonate (**18**). A solution of 0.91 g (3.87 mmol) of tosyl bromide and 0.41 g (3.25 mmol) of allyl crotonate in dichloromethane (36 mL) was irradiated for 24 hours. The solvent was removed under reduced pressure and the oily residue was purified by column chromatography (elution with CH_2Cl_2 and CH_2Cl_2/AcOEt -95:5) to give 0.60 g (51%) of (**18**) as an oil which cristallised after addition of MeOH and had m.p.=48.5-51°C (MeOH). Anal. Calc. for $C_{14}H_{17}O_4SBr$: C, 46.5; H, 4.8; O, 17.7; S, 8.9; Br, 22.1; Found: C, 46.2; H, 4.7; O, 17.0; S, 9.0; Br, 23.1. IR (Nujol) 1711, 1643, 1661, 1412, 1312, 1304, 1278, 1265, 1145, 1088, 1049, 999, 935, 758, 639 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.81 (d, 2H, J=8.0 Hz, Ar), 7.36 (d, 2H, J=8.2 Hz, Ar), 7,00 (m, 1H, =CHCO), 5.82 (dd broad, 1H, J=15.5, 1.6 Hz, =CH-Me), 4.51 (s broad, 3H, O-CH_2, CHBr), 2.43 (s, 3H, Me-Ar), 1.85-1.90 (dd, 3H, J=6.8, 1.5 Hz, Me-C=). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 164.73 (CO), 145.74 (Ar), 144.94 (Me-CH=), 135.54 (Ar), 129.67 (Ar), 127.72 (Ar), 121.20 (=CH-CO), 65.50 (O-CH_2), 59.91 (CH_2-Tos), 39.61 (CHBr), 21.19 (Me-Ar), 17.64 (Me-CH=).

2-Iodo-3-*p*-toluenesulphonylpropyl crotonate (**19**). A solution of 0.31 g (1.1 mmol) of tosyl iodide and 0.41 g (3.25 mmol) of allyl crotonate in dichloromethane (30 mL) was irradiated for 30 minutes. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water and dried ($CaCl_2$). The solvent was removed under reduced pressure and the oily residue was purified by column chromatography (CH_2Cl_2) to give 0.31 g (70%) of (**19**) as a colourless oil. The oil, treated with a few mL of MeOH, gave (**19**) as a white solid, m.p.= 66.5-68.0 °C (MeOH). Anal. Calc. for $C_{14}H_{17}O_4SI$: C, 41.2; H, 4.2; O, 15.7; S, 7.9; I, 31.1; Found: C, 40.9; H, 4.2; O, 15.2; S, 7.9; I, 31.8. IR (Nujol) 1720, 1657, 1585, 1325, 1309, 1302, 1188, 1145, 1103, 976, 748, 681, 542 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.80 (d, 4H, J=8.3 Hz, Ar), 7.38 (d, 4H, J=8.5 Hz, Ar), 7.0 (dq, 1H, J=15.5,

6.9 Hz, =HC-CO), 5.8-6.0 (dq, 1H, J=15.5, 1.7 Hz, =CH-Me), 4.4-4.6 (m, 3H, O-CH_2, CHI), 3.6-3.9 (m, 2H, CH_2-Tos), 2.45 (s, 3H, Me-Ar), 1.8-1.9 (dd, 3H, J=6.9, 1.7 Hz, Me-HC=). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 164.87 (CO), 145.85 (Ar), 145.16 (Ar), 135.56 (Ar), 129.91 (Ar) 127.86 (Ar), 121.47 (=HC-CO), 66.94 (O-CH_2) 61.88 (CH_2-Tos), 21.42 (Me-Ar), 17.86 (Me-HC=), 14.00 (CHI).

2-Bromo-3-*p*-toluenesulphonylpropyl 3-methylcrotonate (**20**). A solution of 3.0 g (12.8 mmol) of tosyl bromide and 1.24 g (8.85 mmol) of allyl 3-methylcrotonate in dichloromethane (100 mL) was irradiated for 19 hours. The solvent was removed under reduced pressure and the oily residue was treated with methanol and left in the refrigerator to give 2.32 g (67%) of (**20**) as a white solid, m.p. 91.5-92.5°C (MeOH). Anal. Calc. for $C_{15}H_{19}O_4SBr$: C,48.0; H, 5.1; S, 8.6; Found: C, 46.9; H, 5.0; S, 8.6. IR (Nujol) 1716, 1650, 1591, 1410, 1312, 1304, 1294, 1273, 1229, 1203, 1144, 1086, 850, 812, 532 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.81 (d, 2H, J=8.3 Hz, Ar), 7.38 (d, 2H, J=8.1 Hz, Ar), 5.67 (s broad, =HC-CO), 4.42-4.51 (m, 3H, O-CH_2, CHBr), 3.84-3.57 (m, 2H, CH_2-Tos), 2.45 (s, 3H, Me-Ar), 2.16 (d, 3H, J=1.2 Hz, *(Z)* Me-C=CO), 1.91 (d, 3H, J=1.2 Hz, *(E)* Me-C=CO). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 165.25 (CO), 158.79 (=CMe_2), 145.34 (Ar), 135.92 (Ar), 130.03 (Ar), 128.15 (Ar), 114.83 (=HC-CO), 63.33 (O-CH_2), 60.51 (CH_2-Tos), 39.81 (CHBr), 27.42 (*(E)* Me-C=CO), 21.60 (Me-Ar), 20.34 (*(Z)* Me C=CO).

2-Iodo-3-*p*-toluenesulphonylpropyl 3-methylcrotonate (**21**). A solution of 2.4 g (8.5 mmol) of tosyl iodide and 0.60 g (4.4 mmol) of allyl 3-methylcrotonate in dichloromethane (50 mL) was irradiated for 30 minutes. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water and dried ($CaCl_2$). The solvent was removed under reduced pressure and the remaining oil was treated with methanol and left in the refrigerator overnight to precipitate 1.21 g (65%) of (**21**) as a white solid, m.p.= 80-81°C (MeOH). Anal. Calc. for $C_{15}H_{19}O_4SI$: C,42.7; H, 4.5; S, 7.6; Found: C, 42.6; H, 4.5; S, 7.7. IR (Nujol) 1717, 1701, 1657, 1592, 1408, 1345, 1312, 1302, 1227, 1142, 1086, 852, 812, 510 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.80 (d, 2H, J=8.2 Hz, Ar), 7.38 (d, 2H, J=8.0 Hz, Ar), 5.68 (s broad, 1H, =HC-CO), 4.38-4.60 (m, 3H, O-CH_2, CHI), 3.55-3.93 (m, 2H, CH_2-Tos), 2.46 (s, 3H, Me-Ar), 2.17 (d, 3H, J= 0.8 Hz, *(Z)* Me-C=CO), 1.92 (d, 3H, J= 0.8 Hz, *(E)* Me-C=CO).^{13}C NMR ($CDCl_3$, 200 MHz) δ 165.20 (CO), 158.61 (=CH-Me), 145.35 (Ar), 135.89 (Ar), 130.10 (Ar), 128.13 (Ar), 114.99 (=HC-CO), 66.74 (O-CH_2), 62.23 (CH_2-Tos), 27.45 (*(E)* Me-C=CO), 21.63 (Me-Ar), 20.40 (*(Z)* Me-C=CO), 14.24 (CHI).

Reaction of methacrylic anhydride with TosBr. A solution of 0.22 g (0.94 mmol) of tosyl bromide and 1.33 g (8.62 mmol) of methacrylic anhydride in carbon tetrachloride (150 mL) was irradiated for 14 hours. After irradiation the solution showed a large quantity of precipitate that was filtered by suction and dried to give 0.80 g of a polymeric material. IR (Nujol) 1800, 1730, 1451, 1386, 1112, 1000 cm^{-1}.

2-Iodo-3-*p*-toluenesulphonylmethacrylic anhydride (**22**). A solution of 7.20 g (25.5 mmol) of tosyl iodide and 1.33 g (8.62 mmol) of methacrylic anhydride in dichloromethane (50 mL) was irradiated for 40 minutes. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water and dried ($CaCl_2$). The solvent was removed under reduced pressure and the remaining oil was treated with CH_2Cl_2/CCl_4 (1:3) to give 2.46 g (40%) of (**22**) as a light yellow solid, m.p.= 113-118°C (dec) ($CHCl_3/CCl_4$, 3:1). IR (Nujol) 1813, 1750, 1591, 1315, 1305, 1292, 1148, 1093, 1084, 1022, 1016, 933, 666 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.86 (d, 4H, J=8.3 Hz, Ar), 7.37 (d, 4H, J=8.0 Hz, Ar), 4.45 (d, 2H, J=14 Hz, CH-Tos), 4.00 (d, 2H, J=14 Hz, CH-Tos), 2.53 (s, 6H, Me-CHI), 2.46 (s, 6H, Me-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 164.36 (CO), 145.51 (Ar), 137.18 (Ar), 130.21 (Ar), 127.95 (Ar), 68.17 (CH_2-Tos), 29.39 (Me-CHI), 29.16 (CHI), 21.66 (Me-Ar).

2-Bromo-3-*p*-toluenesulphonylpropyl acrylate (**23**) and 2-bromo-3-*p*-toluenesulphonylpropyl 2-bromo-3-*p*-toluenesulphonylpropionate (**24**) A solution of 2.97 g (12.6 mmol) of tosyl bromide and 0.35 g (3.2 mmol) of allyl acrylate in dichloromethane (150 mL) was irradiated for 24 hours. The solvent was removed under reduced pressure and the oily residue was column chromatographed (CH_2Cl_2/AcOEt -95:5) to give 0.11g (19%) of (**23**) and 0.35g (11%) of (**24**) as oils.

(**23**) IR (liquid film) 3057, 2966, 2920, 1725, 1594, 1447, 1405, 1312, 1296, 1261, 1180, 1143, 1182, 980, 804 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.84-7.79 (d, 2H, J=8.3 Hz, Ar), 7.41-7.36 (d, 2H, J=8.0 Hz, Ar), 6.45 (dd, 1H, J=17.1, 1.5 Hz, *(Z)* CH=CHCO), 6.20-6.05 (dd, 1H, J=17.1, 10.3 Hz, =CHCO), 5.90 (dd, 1H, 10.3, 1.5 Hz, *(E)* CH=CHCO), 4.53-4.47 (m, 3H, O-CH_2, CHBr), 3.76-3.67 (m, 2H, CH_2-Tos), 2.45 (s, 3H, Me-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 164.92 (CO), 145.40 (Ar), 135.77 (Ar), 131.91 (=CH_2), 130.05 (Ar), 128.05 (Ar), 127.30 (=CHCO), 66.10 (O-CH_2), 60.39 (CH_2-Tos), 39.45 (CHBr), 21.56 (Me-Ar)

(**24**) Anal. Calc. for $C_{20}H_{22}O_6S_2Br_2$: C, 41.3; H, 3.8; O, 16.5; S, 11.0; Br, 27.4; Found: C, 43.3; H, 3.9; O, 16.5; S, 10.8; Br, 25.5. IR (liquid film) 3060, 2980, 2925, 1750, 1596, 1489, 1444, 1400, 1303, 1288, 1191, 1083, 842, 812 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.90-7.72 (m, 4H, Ar), 7.45-7.29 (m, 4H, Ar), 4.64-4.42 (m, 3H, O-CH_2, CHBr), 3.84-3.52 (m, 4H, CH_2-Tos), 2.46 (s, 3H, Me-Ar), 2.45 (s, 3H, Me-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 170.92 (CO), 145.69 (Ar), 145.39 (Ar), 135.72 (Ar), 135.15 (Ar), 130.11 (Ar), 130.03 (Ar), 128.27 (Ar), 128.09 (Ar), 67.64, 67.20 (O-CH_2, diast.), 60.19, 59.99 (CH_2-Tos, diast.), 38.87, 38.55 (O-CH_2CHBr, diast.), 34.0, 34.0 (COCHBr, diast.), 21.54 (Me-Ar)

2-Iodo-3-*p* -toluenesulphonylpropyl 2-iodo-3-*p* -toluenesulphonylacrylate (**25**). A solution of 1.76 g (6.24 mmol) of tosyl iodide and 0.28 g (2.50 mmol) of allyl acrylate in dichlo-

romethane (25 mL) was irradiated for 30 minutes. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water and dried ($CaCl_2$). A T.L.C. (CH_2Cl_2) revealed that some monoadduct remained unreacted; 0.50 g (1.77 mmol) more of tosyl iodide were added and irradiated for further 10 min.. The light red solution was treated as above and the solvent was removed under reduced pressure. Ethanol (2-3 mL) was added to the remaining oil yielding 1.12 g (66%) of (**25**) as a white solid, m.p. 122-124 °C (Ethanol). Anal. Calc. for $C_{20}H_{22}O_6S_2I_2$: C, 35.5; H, 3.3; O, 14.2; S, 9.5; I, 38.4; Found: C, 35.5; H, 3.2; O, 13.8; S, 9.5; I, 38.0. IR (Nujol) 1747, 1594, 1377, 1324, 1304, 1209, 1163, 1143, 1132, 1086, 820, 841, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.72-7.95 (m, 4H, Ar), 7.38 (d, 4H, J=8.0 Hz, Ar), 3.52-4.74 (m, 8H, $\underline{CH_2}$-Tos, O-CH_2, CHI), 2.45 (s, 3H, $\underline{Me}$-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 168.34 (CO), 145.63 (Ar), 135.67 (Ar), 135.09 (Ar), 130.11 (Ar), 130.08 (Ar), 128.20 (Ar), 128.09 (Ar), 69.00, 68.86 (O-CH_2,diast.), 61.69 ($\underline{CH_2}$-Tos), 61.53 ($\underline{CH_2}$-Tos), 21.58 ($\underline{Me}$-Ar), 12.30 ($\underline{CHI}$-O-CH_2), 5.44, 5.33 ($\underline{CHI}$-CO,diast.).

Allyl 2-iodo-3-*p*-toluenesulphonylacrylate (**26**). A solution of 0.85 g (3.01 mmol) of tosyl iodide and 0.56 g (5.0 mmol) of allyl acrylate in dichloromethane (200 mL) was irradiated for 30 min.. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water and dried ($CaCl_2$), and the solvent removed under reduced pressure. The remaining oil was chromatographed in column (CH_2Cl_2) to give a 1st fraction of 0,63 g (32%) of (**26**) as an oil, which decomposed spontaneously. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.75 (d, 2H, J=8.3 Hz, Ar), 7.35 (d, 2H, J=8.0 Hz, Ar), 5.96-5.28 (m, 1H, CH=), 5.41-5.30 (m, 2H, CH_2=), 4.70-4.48 (m, 3H, O-CH_2, CHI), 4.24-4.41 (dd, 1H, J=14.2, 11.7 Hz, $\underline{CH}$-Tos), 3.69-3.60 (dd, 1H, J=14.2, 2.8 Hz, $\underline{CH}$-Tos), 2.42 (s, 3H, $\underline{Me}$-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 168.52 (CO), 144.99 (Ar), 134.91 (Ar), 130.57 (CH=), 129.78 (Ar), 127.78 (Ar), 118.44 (CH_2=), 66.16 (O-CH_2), 61.09 ($\underline{CH_2}$-Tos), 21.17 ($\underline{Me}$-Ar), 6.03 (CHI)

To this oily residue ethyl acetate (5 mL) was added, followed by 1mL (7.2 mmol) of triethylamine dropwise. The ammonium salt precipitated immediately; the solution was stirred for 30 min. at 30-40 °C. After filtration it was diluted with ethyl ether (30 mL), washed with water, dilute solution of HCl, water and dried ($MgSO_4$). The solvent was removed under reduced pressure to give 0.29 g (68%) of the deshydrohalogenated product: *(E)* allyl 3-*p*-toluenesulphonylacrylate (**27**) as an oil.

(E) Allyl 3-*p*-toluenesulphonylacrylate (**27**). A solution of 0.56 g (5.0 mmol) of allyl acrylate and 0.48 g (1.7 mmol) of tosyl iodide in dichloromethane (50 mL) was allowed to react under visible light for 30 minutes. The resulting solution was washed with $Na_2S_2O_3$ (10%) and water, dried ($CaCl_2$) and evaporated under reduced pressure yielding an oil. A solution of this oil in ethyl acetate (5 mL) and 1,0 mL of triethylamine was left 30 min at 35-40°C. The ammonium salt was removed by filtration and the yellow filtrate was dissolved in

dichloromethane (20 mL). After washing with aqueous HCl (5%) and water, the dried ($CaCl_2$) organic layer was evaporated under reduced pressure to give an oil, which was purified by column chromatography (CH_2Cl_2), yielding 0.20 g (44%) of an oil, identified as (**27**). Anal. Calc. for $C_{13}H_{14}O_4S$: C, 58.6; H, 5.3; O, 24.0; S, 12.0; Found: C, 59.1; H, 5.6; O, 23,6; S, 11.7; IR (liquid film) 1728, 1657, 1597, 1495, 1450, 1327, 1298, 1229, 1186, 1167, 1148, 1086, 1018, 992, 833, 812, 725, 707, 644 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.79 (d, 2H, J=8.3 Hz, Ar), 7.37 (d, 2H, J=8.5 Hz, Ar), 7.37 (d, 1H, J=15.2 Hz, =CH-Tos), 6.81, (d, 1H, J=15.2 Hz, COCH=), 5.97-5.81 (m, 1H, CH=), 5.29-5.40 (m, 2H, CH_2=), 4.66 (dt, 2H, J=5.8, 1.3 Hz, O-CH_2), 2.44 (s, 3H, Me-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 162.87 (CO), 145.44 (Ar), 143.55 (=CH-Tos), 135.14 (Ar), 130.88 (CH=), 130.03 (Ar), 129.83 (COCH=), 128.10 (Ar), 119.07 (CH_2=), 66.13 (O-CH_2), 21.40 (Me-Ar).

2-Bromo-3-*p*-toluenesulphonylpropyl 2-bromo-2-methyl-3-*p*-toluenesulphonylpropanoate (**28**). A solution of 2.10 g (8.93 mmol) of tosyl bromide and 0.22 g (1.74 mmol) of allyl methacrylate in dichloromethane (100 mL) was irradiated for 24 hours. The solvent was removed under reduced pressure to give a solid residue (mostly unreacted tosyl bromide). The TsBr was extracted with hot petroleum ether 40-60°C, and the insoluble solid was column chromatographed (CH_2Cl_2/AcOEt 95:5) to give (2nd fraction) 0.16 g (16%) of (**28**) as an oil. IR (liquid film) 1750, 1600, 1462, 1361, 1323, 1305, 1190, 1177, 1148, 993, 816, 768 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.70-7.87 (m, 4H, Ar), 7.30-7.40 (m, 4H, Ar), 3.50-4.72 (m complex, 7H, CH_2-Tos, O-CH_2, CHBr), 2.45 (s, 3H, Me-Ar), 2.43 (s, 3H, Me-Ar), 2.21 (s, 3H, Me-CHBr). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 168.05 (CO), 145.31 (Ar), 136.89 (Ar), 135.72 (Ar), 129.97 (Ar), 128.09 (Ar), 127.75 (Ar), 67.74 (O-CH_2), 65.66 (MeCBr-CH_2-Tos), 60.17 (CHBr-CH_2-Tos), 51.69 (MeCBr), 38.77 (CHBr), 29.96 (Me-CBr), 21.50 (Me-Ar).

2-Iodo-3-*p*-toluenesulphonylpropyl methacrylate (**29**) and Allyl 2-iodo-2-methyl-3-*p*-toluenesulphonylpropanoate (**30**). A solution of 0.85 g (3.01 mmol) of tosyl iodide and 1.14 g (9.05 mmol) of allyl methacrylate in dicholomethane (200 mL) was irradiated for 30 min. After irradiation, the red solution was successively washed with $Na_2S_2O_3$ (10%), water and dried ($CaCl_2$) and the solvent removed under reduced pressure. The remaining oil was chromatographed in column [(CH_2Cl_2/AcOEt -95:5)/Petroleum ether 40-60 °C -2:1] to give (1st fraction) 0.38 g (oil) (37%) of allyl 2-iodo-2-methyl-3-*p*-toluenesulphonylpropanoate (**30**) identified by ^1H and ^{13}C NMR. The ^1H spectra showed the presence of a small amount of dehydrohalogenated product.

(**30**) ^1H NMR ($CDCl_3$, 200 MHz): δ 7.76 (d, 2H, J=8.3 Hz, Ar), 7.35 (d, 2H, J=8.0 Hz, Ar), 6.15-6.76 (m, 1H, CH=), 5.48-5.20 (m, 2H, CH_2=), 4.71-4.62 (m, 2H, O-CH_2),

4.47 (d, 1H, J=6.9 Hz, CH-Tos), 3.97 (d, 1H, J=6.9 Hz, CH-Tos), 2.44 (s, 3H, Me-Cl), 2.43 (s, 3H, Me-Ar). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 170.28 (CO), 144.83 (Ar), 137.23 (Ar), 130.94 (Ar), 127.44 (Ar), 66.57 (CH_2-Tos), 68.31($O-CH_2$) 29.43 (CH_3-Cl), 21.27 (Me-Ar), 12.97 (Cl).

To a solution of this mixture in ethyl acetate (5 mL) triethylamine (1mL) (7.20 mmol) was added dropwise. The ammonium salt precipitated immediately; the solution was stirred for 30 min. at room temperature. After filtration it was diluted with ethyl ether (30 mL), washed with water, dilute solution of HCl and dried ($MgSO_4$). The solvent was removed under reduced pressure to give allyl 3-*p*-toluenesulphonylmethacrylate (mixture of *E, Z* isomers) as an oil. IR (liquid film) 3057, 2914, 1720, 1623, 1594, 1442, 1320, 1300, 1226, 1145, 1112, 1083, 935, 817 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.82 (d, 2H, J=8 0 Hz, Ar), 7.34 (d, 2H, J=8.0 Hz, Ar), 7.25 (s broad, 1H, Tos-CH=), 5.78-6.03 (m, 1H, $CH=CH_2$), 5.18-5.42 (m, 1H, $=CH_2$), 4.65 (d, 2H, J=5.5 Hz, $O-CH_2$), 2.45 (s, 3H, Me-Ar), 2.34 (s, 3H, Me-C=), 2.16 (s, 3H, Me-C=). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 165.17 (CO), 145.08 (Ar), 140.65 (Tos-CH=), 137.61 ($CH=CH_2$), 137.44 (Ar), 131.07 (Me-C=), 129.97 (Ar), 127.59 (Ar), 119.17 ($=CH_2$), 66.58 ($O-CH_2$), 29.53 (Me-C=), (21.53 (Me-Ar), 13.20 (Me-C=).

The 2nd fraction gave 0.20 g of **(29)** as an oil. IR (liquid film) 1709, 1641, 1597, 1401, 1315, 1304, 1294, 1169, 1140, 1080, 947, 895, 810, 746 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.80 (d, 2H, J=8.3 Hz, Ar), 7.38 (d, 2H, J=8.0 Hz, Ar), 6.15 (m, 1H, CH=CHCO *(Z)*), 5.62 (m, 1H, CH=CHCO *(E)*), 4.42-4.66 (m, 3H, $O-CH_2$, CHI), 3.65-3.90 (m, 2H, CH_2-Tos), 2.45 (s, 3H, Me-Ar), 1.95 (m, 3H, Me-C=). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 165.97 (CO), 145.35 (Ar), 135.70 (Me-C=), 135.36 (Ar), 130.08 (Ar), 129.96 (Ar), 126.43 ($=CH_2$), 67.49 ($O-CH_2$), 62.20 (CH_2-Tos), 21.53 (Me-Ar), 18.07 (Me-C=), 13.91 (CHI).

Propyl acrylate **(31)**. To a solution of of triethylamine (23.0 mL, 165 mmol), dried *n*-propanol (7.80 mL, 104 mmol) diethyl ether (70 mL) (dried over sodium), 10.00 mL (123.1 mmol) of acryloil chloride was added, with stirring and cooling (T =0 ^0C). This solution was stirred at room temperature for 16 hours. The ammonium salt was removed by suction filtration and the yellow filtrate was evaporated under reduced pressure. The residue was dissolved in chloroform (50 mL) and washed with aqueous HCl (5%) and water. The organic layer was extracted twice with chloroform, washed with water, dried with $CaCl_2$ and evaporated under reduced pressure (0.1g of hydroquinone was added to avoid polymerization). The crude product was distilled under reduced pressure, yielding 6.52 g (55%) of a colourless liquid, identified as pure propyl acrylate. IR (liquid film) 3024, 2970, 2882, 1726, 1637, 1620, 1410, 1296,1273, 1194, 1062, 987, 964, 812 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.46-6.36 (dd, 1H, J=17.3, 1.7 Hz, *(Z)* HC=CCO), 6.19-6.06 (dd, 1H, J=17.2, 10.2 Hz, =CHCO), 5.85-5.79 (dd, 1H, J=10.2, 1.7 Hz, *(E)* HC=CCO), 4.12

(t, 2H, J=6.7 Hz, O-CH_2), 1.68 (m, 2H, O-$CH_2\underline{CH_2}$), 0.99 (t, 3H, J=1.4 Hz, Me). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 166.21 (CO), 130.25 ($\underline{HC}=CH_2$), 128.58 ($HC=\underline{CH_2}$), 66.00 (O-CH_2), 21.91 (CH_2), 10.27 (Me).

Butyl acrylate (**32**). To a solution of 23.0 mL (165 mmol) of triethylamine and 9.54 mL (104 mmol) of *n*-butanol in dried diethyl ether (70 mL), 10.00 mL (123.1 mmol) of acryloil chloride (caution: vigorous reaction) were added, with stirring and cooling. The solution was refluxed for 16 hours. The ammonium salt was removed by filtration and the yellow filtrate was evaporated under reduced pressure. The residue was dissolved in 50 mL of chloroform and then washed with 50 mL of aqueous HCl (5%). The organic layer was extracted twice with two 25 mL portions of chloroform, washed with water, dried ($CaCl_2$) and then evaporated under reduced pressure (0.1g of hydroquinone was added to avoid polymerization). The impure product was distilled under reduced pressure, yielding 7.12 g (53%) of a colourless liquid, identified as pure butyl acrylate. IR (liquid film) 3040, 2963, 2937, 2876, 1728, 1637, 1622, 1468, 1408, 1296, 1275, 1192, 985, 968, 812 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.45-6.36 (dd, 1H, J=17.3, 1.7 Hz, *(Z)* HC=CCO), 6.19-6.05 (dd, 1H, J=17.3, 10.3 Hz, =CHCO), 5.84-5.78 (dd, 1H, J=10.3, 1.7 Hz, *(E)* HC=CCO) 4.16 (t, 2H, J=6.5 Hz, O-CH_2), 1.66 (m, 2H, O-$CH_2\underline{CH_2}$), 1.40 (m, 2H, $\underline{CH_2}$Me), 0.95 (t, 3H, J=7.2 Hz, Me). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 166.22 (CO), 130.24 (=$\underline{CH}$CO), 128.60 ($\underline{CH_2}$=CH), 64.30 (O-CH_2), 30.59 (O-$CH_2\underline{CH_2}$), 19.06 ($\underline{CH_2}$Me), 13.60 (Me).

Propyl 2-iodo-3-*p*-toluenesulphonylpropanoate (**35**). A solution of 0.72 g (6.3 mmol) of propyl acrylate and 2.00 g (7.09 mmol) of tosyl iodide in 20 mL of dichloromethane was allowed to react under visible light for 30 minutes. The violet solution was washed with $Na_2S_2O_3$ (10%) and water, dried with $CaCl_2$ and evaporated under reduced pressure, yielding 2.42 g (97%) of a yellow oil. This oil was treated with petroleum ether 40-60^{0}C, yielding white cristals of pure (**35**), m.p. 58-59 ^{0}C. Anal. Calc. for $C_{13}H_{17}O_4SI$: C, 39.41; H, 4.32; S, 8.09; Found: C, 39.20; H, 4.20; S, 7.40. IR (Nujol) 1738, 1462, 1377, 1356, 1313, 1300, 1288, 1219, 1165, 1128, 1109, 1084, 752 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.77 (d, 2H, J=8.3 Hz, Ar), 7.37 (d, 2H, J=8.1 Hz, Ar), 4.68-4.61 (dd, 1H, J=11.6, 2.7 Hz, $\underline{CH}$-Tos), 4.25-3.97 (dd, 1H, J=14.1, 11.6 Hz, CHI), 4.01 (t, 2H, J=6.6 Hz, O-CH_2), 3.62-3.54 (dd, 1H, J=14.1, 2.8 Hz, $\underline{CH}$-Tos), 2.46 (s, 3H, $\underline{Me}$Ar), 1.65 (m, 2H, $\underline{CH_2}$Me), 0.99 (t, 3H, J=3.4 Hz, Me). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 169.48 (CO), 145.47 (Ar), 135.41 (Ar), 130.06 (Ar), 129.28 (Ar), 67.97 (O-CH_2), 61.81 ($\underline{CH_2}$-Tos), 21.64 ($\underline{Me}$Ar), 21.48 ($\underline{CH_2}$Me), 10.23 ($CH_2\underline{Me}$), 6.30 (CHI).

Butyl 3-*p*-toluenesulphonyl-2-propenoate (**38**). A solution of 0.83 g (6.48 mmol) of butyl acrylate and 2.02 g (7.16 mmol) of tosyl iodide in dichloromethane (20 mL) was irradiated under visible light for 30 minutes. The violet solution was washed with $Na_2S_2O_3$ (10%) and water, dried ($CaCl_2$) and evaporated under reduced pressure, yielding 2.47 g

(93%) of a pale yellow oil identified by IR and NMR spectroscopy as being butyl 2-iodo-3-*p*-toluenesulphonylpropanoate (**36**). IR (liquid film) 1736, 1597, 1396, 1348, 1321, 1304, 1261, 1207, 1187, 1143, 1086, 815, 752 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.76 (d, 2H, J=8.3 Hz, Ar), 7.37 (d, 2H, J=8.5 Hz, Ar), 4.67-4.60 (dd, 1H, J=11.6, 2.8 Hz, CH-Tos), 4.24-4.11 (dd, 1H, J=14.2, 11.6 Hz, CHI), 4.04 (t, 2H, J=6.5 Hz, O-CH_2), 3.63-3.55 (dd, 1H, J=14.2, 2.8 Hz, CH-Tos), 2.45 (s, 3H, Me-Ar), 1.70-1.54 (m, 2H, O-CH_2CH_2), 1.50-1.31 (m, 2H, CH_2Me),0.94 (t, 3H, J=7.2 Hz, Me). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 169.29 (CO), 145.33 (Ar), 135.28 (Ar), 129.93 (Ar), 128.13 (Ar), 66.09 (O-CH_2), 61.63 (CH_2-Tos), 29.91 (O-CH_2CH_2), 21.51 (Me-Ar), 18.78 (CH_2Me), 13.49 (CH_2Me), 6.30 (CHI).

The oil (2.00g) was dissolved in 10 mL of ethyl acetate and 2.5 mL (15 mmol) of triethylamine were added to the solution. The reaction mixture was stirred for 2 hours at room temperature. The ammonium salt was removed by filtration and the yellow filtrate was dissolved in dichloromethane (20 mL). After washing with aqueous HCl (5%) and water, the dried ($CaCl_2$) organic layer was evaporated under reduced pressure to yield 1.20 g (88%) of a yellow solid, identified as butyl 3-*p*-toluenesulphonyl-2-propenoate (**38**). After recristallization from methanol the product had m.p.= 33-34 ^0C. Anal. Calc. for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.35; Found: C, 59.29; H, 6.49; S, 11.47. IR (Nujol) 1713, 1595, 1462, 1377, 1321, 1307, 1292, 1238, 1176, 1147, 1086, 985, 814, 727, 561 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.80 (d, 2H, J=8.4 Hz, Ar), 7.38 (d, 2H, J=8.0 Hz, Ar), 7.32 (d, 1H, J=15.2 Hz, =CHCO), 6.80 (d, 1H, J=15.1 Hz, =CH-Tos), 4.19 (t, 2H, J=6.5 Hz, O-CH_2), 2.46 (s, 3H, Me-Ar), 1.69-1.60 (m, 2H, O-CH_2CH_2), 1.50-1.30 (m, 2H, CH_2Me), 0.93 (t, 3H, J=7.2 Hz, Me). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 163.56 (CO), 145.59 (Ar), 143.34 (=CH-Tos), 135.38 (Ar), 130.46 (=CHCO), 130.21 (Ar), 128.33 (Ar), 65.78 (O-CH_2), 30.35 (O-CH_2CH_2), 21.66 (Me-Ar), 18.96 (CH_2Me), 13.56 (Me).

Propyl 3-(*p*-toluenesulphonyl)allyl ether (**39**). A solution of 0.63 g (6.28 mmol) of allyl propyl ether and 2.01 g (7.12 mmol) of tosyl iodide in dichloromethane (20 mL) was allowed to react under visible light for 30 minutes. The resulting solution was washed with $Na_2S_2O_3$ (10%) and water, dried ($CaCl_2$) and evaporated under reduced pressure yielding 1.94 g of a yellow oil . A solution of this oil in ethyl acetate (10 mL) was refluxed for 3 hours with 2.5 mL (15 mmol) of triethylamine. The ammonium salt was removed by filtration and the yellow filtrate was dissolved in dichloromethane (20 mL). After washing with aqueous HCl (5%) and water, the dried ($CaCl_2$) organic layer was evaporated under reduced pressure to yield 1.02 g (64%) of a brown oil. The oil (0.42 g) was purified by column chromatography (CH_2Cl_2), yielding 0.26 g (1.01mmol) of a pale yellow oil, identified as propyl 3-*p*-toluenesulphonylallyl ether (**39**). IR (liquid film) 1597, 1446, 1361, 1317, 1304, 1280, 1145, 1086, 1018, 945, 814, 760, 667 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.77 (d, 2H, J=8.3 Hz, Ar), 7.33 (d, 2H, J=8.5 Hz, Ar), 7.01-6.90 (dt, 1H, J=15.0, 3.4 Hz, =CHCH_2),

6.65-6.56 (dt, 1H, J=15.0, 2.1 Hz, =CH-Tos), 4.15 (dd, 2H, J=3.4, 2.1 Hz, =CHCH$_2$), 3.45-3.37 (m, 2H, O-CH$_2$), 2.43 (s, 3H, Me-Ar), 1.62-1.52 (m, 2H, CH$_2$Me), 0.95-0.86 (m, 3H, Me). ^{13}C NMR (CDCl$_3$, 200 MHz): δ 144.21 (Ar), 142.30 (=CH-Tos), 137.30 (Ar), 130.25 (=CHCH$_2$), 129.75 (Ar), 127.60 (Ar), 72.85 (=CHCH$_2$), 68.14 (O-CH$_2$), 22.63 (CH$_2$Me), 21.45 (Me-Ar), 10.37 (Me).

Butyl 3-(*p*-toluenesulphonyl)allyl ether (**40**). A solution of 0.75 g (6.55 mmol) of allyl butyl ether and 2.00 g (7.11 mmol) of tosyl iodide in dichloromethane (20 mL) was allowed to react under visible light for 30 minutes. The resulting violet solution was washed with $Na_2S_2O_3$ (10%) and water, dried with $CaCl_2$ and evaporated under reduced pressure yielding 1.95 g (76%) of a yellow oil which was identified by NMR spectroscopy as butyl 2-iodo-3-*p*-toluenesulphonylpropyl ether (**37**). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.79 (d, 2H, J=8.3 Hz, Ar), 7.37 (d, 2H, J=8.1 Hz, Ar), 4.52-4.38 (m, 1H, CHI), 3.99-3.88 (dd, 1H, J=14.6, 8.1 Hz, CH-Tos), 3.71-3.68 (dd, 2H, J=5.1, 1.9 Hz, CHICH$_2$-O), 3.64-3.54 (dd, 1H, J=14.6, 5.5 Hz, CH-Tos), 3.43 (t, 2H, J=6.5 Hz, O-CH$_2$), 2.45 (s, 3H, Me-Ar), 1.60-1.53 (m, 2H, O-CH$_2$CH$_2$), 1.52-1.35 (m, 2H, CH$_2$Me),0.91 (t, 3H, J=7.1 Hz, Me). ^{13}C NMR (CDCl$_3$, 200 MHz): δ 145.04 (Ar), 136.09 (Ar), 129.91 (Ar), 127.93 (Ar), 73.94 (CHICH$_2$-O), 70.64 (O-CH$_2$), 61.68 (CH$_2$-Tos), 31.36 (O-CH$_2$CH$_2$), 21.51 (Me-Ar), 19.12 (CH$_2$Me), 16.70 (CHI), 13.74 (CH$_2$Me).

A solution of this oil in ethyl acetate (10 mL) was stirred for 30 minutes, at room temperature, with 1.5 mL (10 mmol) of triethylamine. The ammonium salt was removed by filtration and the yellow filtrate was dissolved in dichloromethane (20 mL). After washing with aqueous HCl (5%) and water, the dried ($CaCl_2$) organic layer was evaporated, to yield 0.82 g (61%) of a yellow oil, identified as butyl 3-*p*-toluenesulphonylallyl ether (**40**). IR (liquid film) 1728, 1631, 1597, 1458, 1363, 1317, 1304, 1292, 1280, 1145, 1086, 1018, 814, 760, 706, 665 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.76 (d, 2H, J=8.3 Hz, Ar), 7.33 (d, 2H, J=8.6 Hz, Ar), 7.02-6.91 (dt, 1H, J=15.0, 3.4 Hz, =CHCH$_2$), 6.64-6.55 (dt, 1H, J=15.0, 2.2 Hz, =CH-Tos), 4.15 (dd, 2H, J=3.4, 2.2 Hz, =CHCH$_2$), 3.45 (m, 2H, O-CH$_2$), 2.43 (s, 3H, Me-Ar), 1.63-1.28 (m, 4H, CH$_2$CH$_2$Me), 0.95-0.85 (m, 3H, Me). ^{13}C NMR (CDCl$_3$, 200 MHz): δ 144.22 (Ar), 142.32 (=CH-Tos), 137.30 (Ar), 130.25 (=CHCH$_2$), 129.76 (Ar), 127.60 (Ar), 71.01 (=CHCH$_2$), 68.18 (O-CH$_2$), 31.47 (O-CH$_2$CH$_2$), 21.46 (Me-Ar), 19.09 (CH$_2$Me), 13.72 (Me).

G.L.C. analysis. Relative reactivities were determined by g.l.c. analysis using a Varian 3700 chromatograph, equipped with a flame ionization detector and coupled to a SP 4290 electronic integrator. The column (glass, 2 m 2 mm i. d.) was 3% OV 17 on Gas Chrom Q 100/120 mesh. The nitrogen flow rate was 20 mL/min. The temperature was linearly program-

med: 60°C for 7 min., 60-180 °C, 20 °C/min.. In the case of the competition between propyl acrylate and allyl propyl ether the programming was: 40 °C for 3 min., 40-65 °C, 5 °C/min..

Competition Experiments.: Weighed quantities (0.1-0.4 mmol) of the two olefins were placed in a Pyrex glass tube, envolved in aluminium foil and 2.00 mL of 1% solution of internal standard (*p*- xylene) in dichloromethane, followed by tosyl iodide (0.2-0.8 mmol) were added. The tube was homogenized, stoppered and placed in a thermostat at 30.5 °C. The aluminium foil was removed and the orange solution irradiated under visible light for 1.5 minutes. The reaction was stopped by addition of aqueous potassium iodide followed by $Na_2S_2O_3$ (10%). The colourless organic layer was separated, dried with $CaCl_2$ and analysed by g.l.c..

For each pair of olefins in competition about 10 runs were carried out, with different concentrations of the olefins and of the tosyl iodide.

H.P.L.C. analysis: Relative yields of reaction products were determined by h.p.l.c.. analysis, using a Merck-Hitachi LiChroGraph consisting of a LC-Organizer, L-4200 UV/Vis Detector, L-6200 Intelligent Pump and coupled to a D-2500 Chromato-Integrator. The column (30 cm × 4 mm) was a Varian MicroPak SI-10. The analysis were carried out at $\lambda = 262$ nm, using dichloromethane as eluent.

a) Reaction between TosI and a mixture of butyl acrylate (32) and allyl butyl ether (34)

Weighed quantities (0.18-0.42 mmol) of the two olefins were placed in a Pyrex glass tube, wrapped in an aluminium foil and 2.00 mL of dichloromethane followed by tosyl iodide (0.4-0.6mmol) were added. The tube was homogenized and stoppered. The aluminium foil was removed and the orange solution irradiated under visible light for 20 minutes. The resulting solution was analysed by h.p.l.c.. The chromatograms were compared with those of the isolated monoadducts.

b) Addition of tosyl iodide to allyl methacrylate (9)

Weighed quantities of allyl methacrylate (0.2 mmol) were placed in a Pyrex glass tube and 2.00 mL of dichloromethane, followed by tosyl iodide (0.071-0.21 mmol) were added. The tube was stoppered, the solution homogenized and then irradiated under visible light for 20 minutes. The resulting solution was analysed by h.p.l.c.. The resulting chromatograms showed two peaks of different intensities which were identified as (29) and (30) through comparison with the isolated monoadducts.

c) Addition of tosyl iodide to allyl acrylate (8)

To a solution of allyl acrylate (0.2 mmol) in 2.00 mL of dichloromethane was added about 0.07 mmol of tosyl iodide. The solution was irradiated under visible light for 30 minutes. An

alliquot of this solution was diluted with dichloromethane and analysed by h.p.l.c.. The chromatogram showed two peaks. The first one was identified as **(26)**, after dehydrohalogenation with TEA and comparison with the previously isolated dehydrohalogenated product **(27)**. The second peak was identified as **(25)** after comparison with the isolated product.

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