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RADICAL CHAIN CYCLIZATION OF ALLYLIC COMPOUNDS

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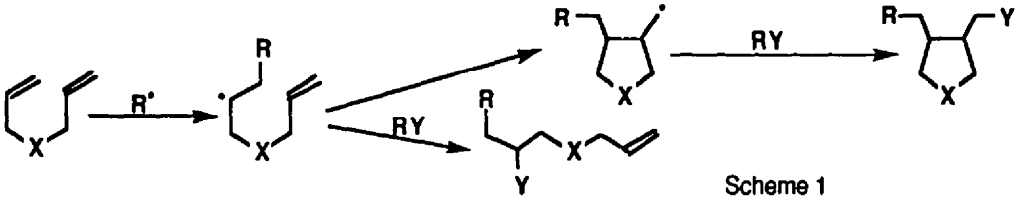
Abstract - The light induced additions of tosyl iodide and tosyl bromide to some diallylic compounds and dienes are studied. Cyclizations occurs in some cases but the yields are quite small. Results are discussed on the grounds of free radical cyclization.

INTRODUCTION

The formation of ring systems through radical cyclization is a very important and current synthetic tool. Chain reactions are specially important in synthesis since the yields and rates are generally high. 1,6-Dienes (**1**) have extensively been used to produce five and six member rings *via* radical chain addition to one double bond followed by intramolecular addition to the other double bond (Scheme 1).



Scheme 1

This process does not need the use of tin compounds to generate the radical and may be used to yield cyclic compounds in large scale. Arenesulphonyl halides have been sucessfully used in this way (1) yielding five and six member rings with easily functionalized substituents (halogen atoms and sulphonyl groups).

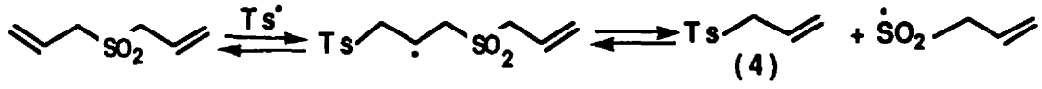
We report here the results of the light induced addition of tosyl iodide (TsI) and tosyl bromide (TsBr) to several diallylic compounds (diallyl sulphide, **1a**; diallyl disulphide, **1b**; diallyl sulphone, **1c**) and other dienes (hexa-1,5-diene, **1d**; allyl methacrylate, **3**) at room temperature under visible light.

RESULTS AND DISCUSSION

Diallyl sulphide (**1a**) reacts with TsBr under visible light, in dichloromethane, to give the tetrahydrothiophene derivative (**2a**,*cis*) in low yield (11%). This was then converted to the corresponding iodine derivative (**2b**,*cis*) that could not be prepared directly from TsI and diallyl sulphide. The usual tendency to form the *cis* isomer was again found (1,2). From the

reaction of diallyl disulphide and TsI no reaction products could be isolated from the complex reaction mixture. With TsBr, after 24 hours of irradiation, no addition products could be detected in the reaction mixture, the unchanged olefin being recovered.

Diallyl sulphone(**1c**), prepared by oxidation of (**1a**) with hydrogen peroxide, reacts with TsBr to yield the cyclic sulphone (**2c**, 40%) in a *cis/trans* ratio of about 1.2/1, as well as of allyl *p*-tolyl sulphone (**4**, 25%), whose presence is the result of the reversibility of the addition of arenesulphonyl radicals to double bonds (3) (Scheme 2).



Scheme 2

The addition of TsI to diallyl sulphone (**1c**) gave only 11% of the cyclic sulphone (**2d**) (the *cis/trans* ratio was about 1.2/1). The bisadduct (**5**) and the disulphone (**6**) were also obtained (23% and 9% yields, respectively). The disulphone (**6**) may result from the addition of TsI to allyl *p*-tolyl sulphone (**4**) which, although not isolated in this reaction, was isolated in the reaction with TsBr. The decrease of stereospecificity in the additions of TsBr and TsI to diallyl disulphone is unexpected (4) since the energy difference of the two chair-like transition states (Fig.1) must be bigger than in the case of diallyl sulphide and diallyl ether (1).

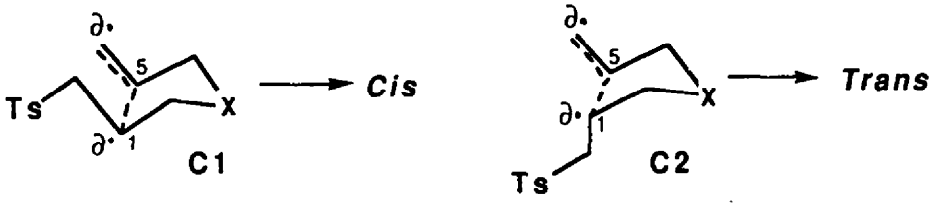


Fig. 1 - Transition states for radical exo-cyclization

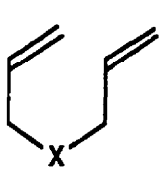
Some studies with thiane 1-oxide (5a) and cyclic thiosulphonates (5b) show a preference for 1-axial conformation that is caused by an attractive 1,3(or 5)-interaction between the oxygen and the 3-axial proton. Replacement of this axial proton by a methyl group make the interaction repulsive and the oxide prefers the equatorial conformation. Under these circunstances the conformation C2 (Fig. 1) should be less stable than conformation C1, unless any attractive interaction between the oxygen and the acidic protons of $TsCH_2$ may arise.

The low yields of cyclization products may be the result of the bigger size of the heteroatom X (S>O)(6). The presence of iodine and bromine in the reaction mixture may also cause complications due to the formation of sulfonium ions in the case of diallyl-sulphide and -disulphide. However, the cyclic sulphide (**2b**) shows no alteration when left in the n.m.r. tube for 45 days in the presence of iodine.

Hexa-1,5-diene (**1d**) gave no cyclic products even under conditions of high dilution; similar

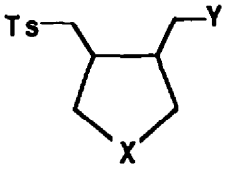
results were obtained with other radicals (7) and they are consistent with the stereoelectronic requirements of the radical cyclization (8). Both the monoadduct (7) and the bisadduct (8) were formed and the formation of the monoadduct could be supressed by using an excess of olefin. Products (7) and (8) were converted into derivatives (9) and (10) by dehydroiodation (with triethylamine) and reduction (with sodium tetrahydroborate).

TsI reacts with allyl methacrylate (3) across the allylic and the acrylic double bonds but no cyclization could be detected. The relative reactivity of these bonds (allylic/acrylic) is about 1.3/1. The smaller reactivity of the acrylic double bond shows that the unfavourable polar effect of the carbonyl group (sulphonyl radicals behave electrophilically) is more important than the favourable delocalization of the unpaired electron over the carbonyl. When the tosyl radical adds to the allylic double bond, the *exo* cyclization is slowed down due to steric hindrance of the methyl group. Either the *exo* or the *endo* cyclizations are not fast enough to compete with the iodine



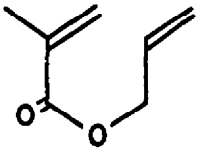
(1)

a: X=S
b: S=S-S
c: X=SO_2
d: X= -



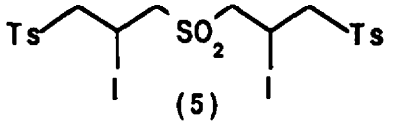
(2)

a: X=S; Y=Br
b: X=S; Y=I
c: X=SO_2; Y=Br
d: X=SO_2; Y=I

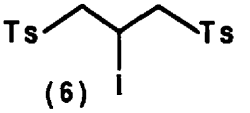


(3)

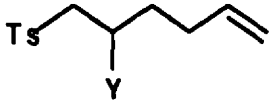
(4)



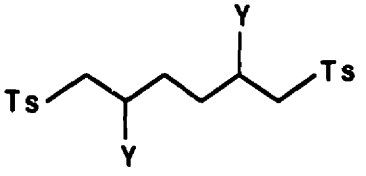
(5)



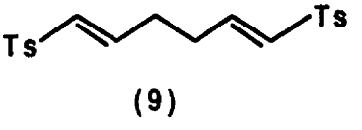
(6)



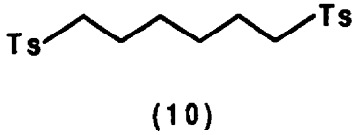
(7) a: Y=Br; b: Y=I



(8) a: Y=Br; b: Y=I



(9)



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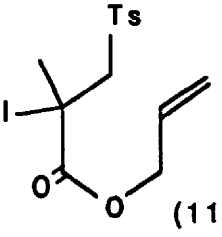

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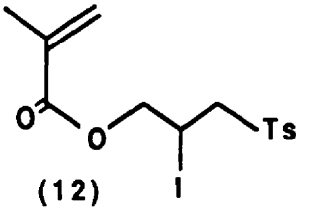

(12)

abstraction from TsI. When Ts· adds to the acrylic double bond, the presence of the alpha methyl group should improve the *exo* cyclization. The inspection of models reveals that the C1-C5 distances in the chair-like transition states of diallyl ether and (3) are similar. However, in the case of (3), the delocalization of the unpaired electron over the carbonyl group twists the C1-C2 bond and so the SOMO is unable to overlap with the π or π^* orbitals of the olefinic system. As before, the cyclization can not compete with the iodine abstraction from TsI. Further studies are in progress. Results of all the reactions are summarized in Table 1.

Table 1 - Reaction products, yields and reaction conditions of the the addition of TsBr and TsI to dienes.

Diene	Y in TsY	Reaction products Cyclic	Acyclic	cis/trans	% Yield	Obs.
Diallyl sulphide (1a)	Br	(2a)		100/0	11%	6 h, hν1(*)
	I	(2b)		100/0	76%	(2a) + NaI 30 min
Diallyl disulphide(1b)	Br					16h, hν1
	I					30 min, hν1
Diallyl sulphone (1c)	Br	(2c)		1.2/1(**)	40%	24 h, hν1
			(4)		25%	
	I	(2d)		1.3/1(**)	11%	40 min, hν1
				(5)	23%	
				(6)	9%	
Hexa-1,5-diene (1d)	Br	0		(7a)	100%	7h, hν1 TsBr/(1d)=1/8
		0		(8a)	55%	(7a) + TsBr, hν1
	I	0		(7b)	58%	TsI/(1d)=1/2
		0		(8b)	22%	10 min, hν2
	I	0		(7b)	98%	15 min, hν2 Ts/(1d)=1/8
				(8b)	68%	(7b) + TsI, hν2
Allyl methacrylate (3)	I	0	(11)		15%(**)	30 min, hν2
			(12)		19%	

(*) hν1 = Philips HP/T 200 w lamp; hν2 = Sunlight. (**) Estimated by NMR.

EXPERIMENTAL

Materials. Tosyl iodide and -bromide were prepared from sodium toluene-p-sulphinate (9). Diallyl sulphide (Aldrich), diallyl disulphide (Aldrich), hexa-1,5-diene (Aldrich), allyl methacrylate (Aldrich), other chemicals, and solvents (good grade commercial products) were

used without further purification. Diallyl sulphone was prepared by oxidation of diallyl disulphide with hydrogen peroxide, as described below. IR and NMR spectra were recorded on a Philips PU 9800 spectrophoptometer and Bruker AC-200 spectrometer, respectively. Mass spectra were recorded on a Kratos MS 25RF instrument, at 70 eV.

Diallyl sulphone (1c). To a solution of 5.99 g (52 mmol) of diallyl sulphide in 40 ml of acetic acid, 17 ml of hydrogen peroxide (30%) were added over a period of 5 minutes. The resulting solution was refluxed for 50 min. After dilution with 200 mL of water, $NaHCO_3$ was added to neutralize the acid, and the organic layer extracted with 3x75 mL of dichloromethane. The combined extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure to give 5.9 g (40 mmol) of a colourless liquid. IR (liquid film) 1639, 1423, 1398, 1317, 1292, 1132, 1090, 993, 939, 873, 785, 640 cm^{-1}; ^{1}H-RMN($CDCl_3$, 200 MHz) ∂ 5.9(m, 2H, CH), 5.4(m, 4H, CH_2=), 3.7(d, 4H, J=8Hz, CH_2SO_2).

3-Bromomethyl-4-*p*-tolylsulphonylmethyltetrahydrothiofen(*cis*)(2a). A solution of 1.75 g (7.5 mmol) of tosyl bromide and 0.71 g (6.11mmol) of diallyl sulphide in 100 mL of dichloromethane was irradiated under visible light (Philips HP/T 200 w lamp) for 24 hours. After removing the solvent under reduced pressure the remaining oil was chromatographed (column) over silica-gel (60, Merck, Art. 7754, 70-230 mesh)(dichloromethane-ethyl acetate,95:5). The first fractions gave 0.4 g of an oil almost diallyl sulphide. The others fractions were an oil which, treated with MeOH and left in the refrigerator overnight, gave 0.24 g of a white solid. After recrystallisation from MeOH the product had a m.p. 123-4 °C. Anal. Calc. for $C_{13}H_{17}S_2O_2Br$: C,44.72; H,4.87; S,18.36; O,9.17; Br,22.88; Found: C,44.98; H,4.93; S,18.44; O,9.21; Br,22.44; IR (Nujol) 1590, 1420, 1296, 1288, 1159, 1086, 817, 802, 779, 723, 675, 663 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) ∂ 7.80(d, 2H, J=8 Hz, Ar), 7.37 (d, 2H, J=8 Hz, Ar), 2.6-3.5 (m, 10 H, CH_2SO_2 CH_2; CH_2Ts; CH_2Br; CH-CH), 2.47 (s, 3H, Me-Ar) ; ^{13}C-RMN ($CDCl_3$) ∂ 144.95 (Ar), 136.43 (Ar), 130.06 (Ar), 128.04 (Ar), 54.2 (CH_2-SO_2), 48.90 (CH- CH_2Br), 40.31 (CH-CH_2Ts), 34.28 (S-CH_2), 33.30 (S-CH_2), 30.0 (CH_2Br), 21.66 (Me-Ar); Mass spectrum, *m/e* (relative intensity) 350 and 348 (M^+,15 and 14.8),269(15),194(49),157(36),139(14),113(86),112(88),99(100),91(76),79(57) 67(43), 41(77).

3-Iodomethyl-4-(*p*-tolylsulphonylmethyl)tetrahydrothiofen (*cis*) (2b). 1.5 g (10.14 mmol) of sodium iodide were added to a solution of 0.60 g (1.71 mmol) of (**2a**) in 15 mL of acetone, and the mixture refluxed for 6h. The mixture was filtered and the filtrate evaporated in vacuo. The remaining product was treated with dichloromethane, filtered and the filtrate evaporated under reduced pressure to give 0.55 g (1.3 mmol) of a pale yellow solid (**2b**). After recrystallization from methanol this product had m.p. 109-10 °C. Anal. Calc. for $C_{13}H_{17}S_2O_2I$: C,39.41; H,4.29; S,16.19; O,8.08; Br,32.03; Found: C,39.28; H,4.34; S,16.19; O,7.75; Br,32.44; IR (Nujol) 1600, 1310, 1300, 1120, 1090, 830, 810, 800, 770, 650 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) ∂ 7.80(d, 2H, J=8 Hz, Ar), 7.38 (d, 2H, J=8 Hz, Ar), 2.51-3.3 (m, 10 H, CH_2SO_2 CH_2; CH_2Ts; CH_2Br; CH-CH), 2.47 (s, 3H, CH_3-Ar); ^{13}C-RMN ($CDCl_3$) ∂ 144.95 (Ar), 136.45 (Ar),130.08(Ar),128.07 (Ar), 54.07 (CH_2-SO_2),49.49 (CH-CH_2Br), 40.83 (CH-CH_2Ts), 34.48 (S-CH_2), 34.00 (S-CH_2), 21.66 (CH_3-Ar); 2.07 (CH_2I). Mass

spectrum, *m/e* (relative Intensity) 396(M^+,15),269(29),240(12),192(11),157(19), 139(10),113(100), 99(39), 91(59), 79(43), 67(30), 41(56).

3-Bromomethyl-4-*p*-tolylsulphonylmethyltetrahydrothiofen-di-S-oxide(cis and trans) (2c). A solution of 2.63 g (12.02 mmol) of tosyl bromide and 1.25 g (8.25 mmol) of diallyl sulphone in 90 mL of dichloromethane was irradiated under visible light (Philips HP/T 200 w lamp) for 24 hours. After removing the solvent under reduced pressure the remaining oil was chromatographed (column) over silica-gel (60, Merck,Art. 7754, 70-230 mesh) (dichloromethane-ethyl acetate,95:5) to give 0.96 g of a white solid whose TLC (silica-gel, dichloromethane-ethyl acetate,95:5) showed two spots. A new passage of this material through the same type .of column gave 0.40 g of (**2c**)(*cis*), as a white solid m.p.182-184 °C (after recrystallisation from MeOH-CH_2Cl_2,3:1) and 0.22 g of (**2c**)(*trans*) as a white solid m.p. 170.5-171.5 °C.(MeOH-Acetone, 4:1).

(**2c**,*cis*): IR (Nujol) 1590, 1302, 1290, 1280, 1176, 1145, 1118, 1105, 1087, 821, 815, 765, 692, 663 cm^{-1}; ^{1}H-NMR (DMSO, 200 MHz) ∂ 7.81(d, 2H, J=8 Hz, Ar), 7.50 (d, 2H, J=8 Hz, Ar), 2.7-3.7 (m, 10 H, $CH_2SO_2CH_2$; CH_2Ts; CH_2Br; CH-CH), 2.43 (s, 3H, Me-Ar); ^{13}C-RMN (DMSO) ∂ 144.79 (Ar), 135.86 (Ar), 130.08 (Ar), 127.77 (Ar), 54.32 (CH_2-SO_2), 54.21 (CH_2-SO_2), 41.59 (CH-CH_2Br), 33.53 (CH-CH_2Ts), 31.85 (CH_2Br) 21.10 (Me-Ar); Mass spectrum, *m/e* (relative intensity) 382 and 380 (M^+, 2.6 and 1.9), 301(4), 227(53.4), 225(52.8),197(39),155(35), 139(16), 119(9), 91(100), 81(71), 64(39), 41(80).

(**2c**,*trans*): IR (Nujol) 1590, 1317, 1311, 1304, 1288, 1246, 1213, 1143, 1132, 1126, 1086, 850, 810, 758, 650 cm^{-1}; ^{1}H-NMR (DMSO, 200 MHz) ∂ 7.82(d, 2H, J=8 Hz, Ar), 7.49(d, 2H, J=8 Hz, Ar), 2.47-4.0 (m, 10H, $CH_2SO_2CH_2$; CH_2Ts; CH_2Br; CH-CH), 2.40 (s,3H, Me-Ar); ^{13}C-RMN (DMSO) ∂ 144.71 (Ar), 135.82 (Ar), 129.96 (Ar), 127.68 (Ar), 56.10 (CH_2-SO_2), 55.40 (CH_2-SO_2), 53.62 (CH_2-Ts), 41.26 (CH-CH_2Br), 34.44 (CH-CH_2Ts), 33.71(CH_2Br), 21.05 (Me-Ar); Mass spectrum, *m/e* (relative intensity) 382 and 380 (M^+,0.42 and 0.52), 301(9), 227(5.5), 225(4.6),197(8),155(47.1), 139(21.6), 119(3.1), 91(100), 81(19), 64(11.1), 41(61).

Allyl-*p*-tolylsulphone(4). A solution of 2.55 g (11.65 mmol) of tosyl bromide and 1.25 g (8.25 mmol) of diallyl sulphone in 90 mL of dichloromethane was irradiated under visible light (Philips HP/T 200 w lamp) for 24 hours. After removing the solvent under reduced pressure the remaining oil was treated with 2 mL of MeOH and cooled; the precipitate (cyclic product, 2c) was recovered by filtration and the filtrate evaporated under reduced pressure to give an oil which was chromatographed (column) over silica-gel (60, Merck, Art. 7754, 70-230 mesh)(dichloromethane-ethyl acetate,95:5). The first fractions gave 0.41 g (25%) of (4) as an oil . This compound was characterized by comparison with an authentical sample prepared (10) by reaction of sodium *p*-toluenesulphinate with allyl bromide (the product was recrystallised from ethanol and had m.p. 52-54 °C; the yield was 52% and its ^{13}C and ^{1}H NMR spectra were identical with those obtained from the oil). Anal. Calc. for $C_{10}H_{12}SO_2$: C,61.23; H,6.12; S,16.34; O,16.31; Found: C,61.40; H,6.21; S,16.38; O,16.01; IR (Nujol) 1600, 1590, 1377, 1317, 1294, 1147,1082, 989, 937, 823, 810, 777, 644 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz) ∂ 7.74 (d, 2H, J= 8 Hz, Ar), 7.33 (d, 2H, J=8 Hz, Ar), 5.76 (m, 1H, CH=), 5.31(dxd,1H, J=9.6 Hz, =CH *cis*), 5.15(d, 1H, J=17,1 Hz, =CH *trans*), 3.80 (d,2H, J=7.3 Hz,

CH_2-Ts), 2.43 (s, 3H, Me-Ar). ^{13}C-RMN ($CDCl_3$) ∂ 144.07(Ar),134.96(Ar),129.09 (Ar),127.74 (Ar), 124.29 (CH=), 123.81 (CH_2=), 60.05 (CH_2-Ts), 20.91 (Me-Ar).

3-Iodomethyl-4-*p*-tolylsulphonylmethyl)tetrahydrothiofen-di-S-oxide(*cis* and *trans*)(2d). To a solution of 0.5 g (3.4 mmol) of diallylsulphone in 400 mL of dichloromethane 1.2 g (4.2 mmol) of tosyl iodide was added gradually under visible light (Philips HP/T 200 w lamp) for 20 minutes. An additional solution of 0.5 g (3.4 mmol) of diallyl sulphone and 1.2 g (4.24 mmol) of tosyl iodide was added and this solution stood for 20 minutes more. The red solution (Port Wine colour) was successively washed with 10% aqueous sodium thiosulphate and water, dried ($CaCl_2$) and the solvent removed under reduced pressure. The oil residue was chromatographed (column) over silica-gel (60, Merck, Art. 7754, 70-230 mesh)(dichloromethane-ethyl acetate,95:5) to give 0.34 g (11%) of a solid characterized as (**2d**,*cis* +*trans*) m.p. 159-160 °C (recrystallised from methanol-dichloromethane, 3:1). Anal. Calc. for $C_{13}H_{17}S_2O_4I$: C,36.47; H,3.97; S,14.98; O,14.94; I,29.64; Found: C,36.57; H,3.99; S,14.93 O,14.92; I,29.59; IR (Nujol)1590, 1313, 1304, 1290, 1271, 1246, 1188, 1140, 1122, 1086, 810, 630 cm^{-1}; ^{1}H-NMR (DMSO, 200 MHz) ∂ 7.81(d, 2H, J = 8Hz, Ar), 7.44 (d, 2H, J=8Hz, Ar), 2.7-3.7 (m, 10 H, CH-CH), 2.46 (s,3H, Me-Ar); ^{13}C-RMN (DMSO) ∂ 144.57 (Ar), 135.56 (Ar), 129.64 (Ar), 127.5 (Ar), 55.7 (CH_2-SO_2,*cis*), 56.49 (CH_2-SO_2,*trans*), 55.47 (CH_2-SO_2,*cis,trans*), 52.98 (CH_2-Ts,*cis*), 54.35 (CH_2-Ts,*trans*), 40.9 (CH-CH_2I,*cis*), 41.97 (CH-CH_2I, *trans*), 34.01(CH-CH_2Ts, *cis*), 35.4 (CH-CH_2Ts, *trans*), 21.05 (Me-Ar), 3.48 (CH_2I, *cis*), 7.85 (CH_2I, *trans*).

Bis(2-iodo-3-*p*-tolylsulphonylpropyl)sulphone (5). To a solution of 1.0 g (6.8 mmol) of diallylsulphone in 20 mL of dichloromethane, 2.3 g (8.14 mmol) of tosyl iodide were added. The resulting solution was irradiated under visible light (Philips HP/T 200 w lamp) for 40 minutes. The residue was treated with MeOH and left in the refrigerator. The product obtained (1.11g) was recrystallised from MeOH (with a few drops of acetone) to give a white solid m.p. 197 °C. Anal. Calc. for $C_{20}H_{24}S_3O_6I_2$: C,33.83; H,3.38; S,13.54; O,13.51; I,35.74; Found: C,31.64; H,3.21; S,13.33; O,12.1; I,39.72; IR (Nujol) 1590, 1402, 1317, 1305, 1288, 1147, 1124, 1086, 815, 748, 673, 665 cm^{-1}; ^{1}H-RMN (DMSO, 200 MHz) ∂ 7.82(d, 2H, J=8 Hz, Ar), 7.50 (d, 2H, J=8 Hz, Ar), 4.3-4.5(m, 2H, CH-I), 3.9-4.2 (m, 8H CH_2SO_2 CH_2; CH_2Ts), 2.43 (s, 3H, Me-Ar); ^{13}C-RMN (DMSO) ∂ 144.97 (Ar), 135.92 (Ar), 130.01 (Ar), 127.91 (Ar), 61.72 (CH_2-Ts), 60.96 (CH_2-SO_2), 60.72 (CH_2-SO_2), 21.10 (Me-Ar), 2.56 (CH-I), 2.25 (CH-I).

2-Iodo-1,3-bis(*p*-tolylsulphonyl)propane (6). To a solution of 0.5 g (3.4 mmol) of diallyl sulphone in 30 mL of dichloromethane 1.15 g (4.07 mmol) of tosyl iodide was added in four portions of about 0.25 g, under irradiation of visible light (Philips HP/T 200W lamp). The solution was then irradiated for 40 minutes. After irradiation, the red solution (Port Wine colour) was successively washed with 10% aqueous sodium thiosulphate and water, dried ($CaCl_2$) and the solvent removed under reduced pressure. The oil residue was chromatographed (column) over silica-gel (60, Merck, Art.7754, 70-230 mesh)(dichloromethane-ethyl acetate,95:5), and gave 0.15 g of a solid which was recrystallised from methanol and identified

by comparaison with an authentic sample prepared by reaction of 1.9 g (6.7 mmol) of tosyl iodide with 1.0 g (5.1 mmol) of sulphone (**4**), under visible light (20 minutes). After the work-up described above this gave a solid which, after recrystallisation from ethanol-acetone(4:1), yielded 1.46 g of (**6**) as white cristals m.p. 156-157 °C. Anal. Calc. for $C_{17}H_{19}S_2O_4I$: C,42.70; H,3.97; S,113.40; O,13.38; I,26.54; Found: C,42.35; H,4.02; S,13.44; O,13,74; I,26.45; IR (Nujol) 1590, 1320, 1300, 1290, 1170, 1130, 1120, 1080, 880, 815, 740 cm^{-1}.^{1}H-RMN ($CDCl_3$, 200 MHz) ∂ 7.77(d, 2H, J=8 Hz, Ar), 7.38(d, 2H, J=8 Hz, Ar), 4.42(q, 1H, J=6.8 Hz, CH-I), 4.12(dxd, 2H, J=15, 7 Hz, CH-Tos), 3.74(dxd, 2H, J=15,6 Hz, CH-Tos), 2.46 (s, 3H, Me-Ar); ^{13}C-RMN ($CDCl_3$) ∂ 145.49 (Ar), 135.49 (Ar), 130.12 (Ar), 128.19 (Ar), 63.21(CH_2-Tos), 20.91 (Me-Ar), 2.36 (CH-I).

5-Bromo-6-*p*-tolylsulphonyl-hex-1-ene (7a). A solution of 2,5 g (10.6 mmol) of tosyl bromide and 10.0 mL (84.2 mmol) of hexa-1,5-diene in 320 mL of dichloromethane was irradiated for 7 hours under visible light (Philips HP/T 200 w lamp). The solvent and the excess of diene were removed under reduced pressure, leaving 3.63 g of an oil that was identified as (**7a**) contaminated with a small amount of bisadduct (**8a**). The oil (1.0 g) was purified by column chromatography (silica gel 60, Merck, Art. 7754, 70-230 mesh) yielding 0.92 g of pure (**7a**). Anal. Calc. for $C_{13}H_{17}BrO_2S$: C,49.22; H,5.40; O,10.09; S,10.11; Found: C,48.97; H,5.42; O,9.86; S,10.21; IR (liquid film) 3533, 3077, 2973, 2921, 2862,. 1642, 1597, 1493, 1445, 1404, 1329, 1303, 1292,1146, 1087, 1040, 1019, 996, 917, 872, 844, 816, 760, 748, 682, 666, 632 cm^{-1}; ^{13}C-NMR ($CDCl_3$) ∂ 145.13(Ar), 136.14(Ar), 136.10(-CH=),129.94(Ar),127.95(Ar),116.12(=CH_2), 65.79(CH_2S), 44.56(CHBr),37.13 (CH_2),31.03 (CH_2), 21.52(Me,Ar); Mass spectrum,*m/e* (relative intensity) 317 and 319(M^+, <0.3%), 157(27), 139(8), 91(8), 81(100), 65(18), 53(10), 41(36).

5-Iodo-6-*p*-tolylsulphonyl-hex-1-ene (7b). A solution of 3.0 g (10.7 mmol) of tosyl iodide and 10.0 mL (84.2 mmol) of hexa-1,5-diene in 350 mL of dichloromethane was left under sunlight for 15 minutes. The colourless solution was evaporated under reduced pressure, yielding 3.78 g of colourless oil that was purified by silica gel chromatography. IR (liquid film)3065, 2977, 2847, 1922, 1814, 1640, 1596, 1495, 1445, 1403, 1364, 1318, 1303, 1291, 1266, 1147, 1087, 1018, 995, 919, 842, , 817, 752, 738, 702, 677, 632 cm^{-1}; ^{1}H-RMN ($CDCl_3$, 200 MHz) ∂ 7.78 (d, J=8 Hz, 2H, Ar), 7.37 (d, J=8 Hz, 2H, Ar), 5.9-5.6 (m, 1H, =CH), 5.07 (d, J=16 Hz, 1H, =C$\overset{H}{<}$), 5.02 (d, J=16 Hz, 1H, =C$\overset{H}{<}$),4.3-4.5 (m, 1H, CHI), 3.7-3.9 (m, 2H, CH_2S), 2.45 (s, 3H, MeAr), 1.8-2.4 (m, 4H, CH_2-CH_2); ^{13}C-NMR ($CDCl_3$) ∂ 144.90(Ar), 135.89(Ar), 135.67(CH=), 129.80(Ar), 127.65(Ar), 115.97(=CH_2), 65.36(CH_2S), 37.63(CH_2), 33.22(CH_2), 21.4(CHI), 21.4(MeAr).

2,5-Dibromo-bis(*p*-tolylsulphonyl)hexane (8a). A solution of 1.27 g (5.4 mmol) of (**7a**) in 10 mL of dichloromethane was irradiated for 7 hours (Philips HP/T 200 w lamp) during which some long crystals of (**8a**) deposited (0.95 g). The filtrate solution was evaporated under vacuo and a solid residue was left; after being washed with ethanol, 0.70 g of (**8a**) were obtained. The combined solids were recrystallised from 200 mL of ethanol/acetone (1/2), yielding crystals m.p. 126-7 °C; IR (Nujol) 1595, 1406, 1315, 1290, 1246, 1150, 1140,

1118, 1085, 1032, 1018, 972, 855, 819, 808, 791, 741, 689, 679, 665 cm^{-1};^{1}H-NMR ($CDCl_3$,200 MHz) ∂ 7.82 (d, 2H, J=8 Hz, Ar), 7.39 (d, 2H, J=8 Hz, Ar),4.35 (m, 1H, CHBr), 3.66 (m, 2H, CH_2S), 2.47 (s, 3H, MeAr), 2.0-2.2 (m, 2H, CH_2-CH_2); ^{13}C-NMR ($CDCl_3$) ∂ 145.77(Ar), 136.12(Ar), 130.23(Ar), 128.16(Ar), 63.60(CH_2S), 43.92(CHBr), 35.48(CH_2); Mass spectrum,*m/e* (relative intensity) 552(M^+, <1%), 390(12), 157(24), 139(32), 91(65), 80(61), 65(21), 55(17), 45(100).

2,5-Diiodo-1,6-bis(*p*-tolylsulphonyl)hexane(8b). This bisadduct is formed directly from the reaction of tosyl iodide (3.45 g, 12.2 mmol) and hexa-1,5-diene (2.5 mL, 21.1 mmol) in dichloromethane (30 mL) under sunlight for 10 minutes. After removing the solvent and excess of olefin, ethanol(50 mL) was added to the residue and the mixture left in the refrigerator. The crystals obtained (0.85 g, 22%) were recrystallised from acetone and had m.p. 200-2 °C (dec.). The same bisadduct (1.21g, 68%) was obtained by addition of tosyl iodide (0.9 g, 3.2 mmol) to the monoadduct (**7a**)(1.0 g, 2.7 mmol) in dichloromethane (20 mL) under sunlight. IR (Nujol) 1594, 1403, 1316, 1304, 1292, 1275, 1233, 1149, 1128, 1086, 1018, 819, 797, 782, 733, 683, 673 cm^{-1}; ^{1}H-NMR ($CDCl_3$,200 MHz) ∂ 7.83 (d, 2H, J=8 Hz, Ar), 7.82 (d, 2H, J=8 Hz, Ar'), 7.40 (d,d, 4H, J=8 Hz, Ar+Ar'), 4.43 (m, 2H, CHI), 3.76 and 3.75 (d,d, 4H, J=6,8 Hz, CH_2S-*meso*, CH_2S-*d,l*), 2.47 (s, 6H, MeAr + MeAr'), 1.9-2.3 (m, 4H, CH_2--CH_2); ^{13}C-NMR ($CDCl_3$) 145.43(Ar), 136.11(Ar), 130.28(Ar), 129.11(Ar), 65.47 (CH_2S), 38.7 and 38.5 (CH_2-CH_2,*meso* + *d,l*), 21.71(MeAr), 19.21(CHI); Mass spectrum, *m/e* (relative intensity) 389 (10%), 235(8), 157(28),139(43),128(71), 91(100), 81(46), 65(33), 51(2), 41(26). The ethanolic filtrate from which the solid (**8b**) was separated, gave an oil as residue. Its IR spectrum was identical with that of the monoadduct (**7b**).

1,6-Bis(*p*-tolylsulphonyl)hexa-1,5-diene(9). A solution of 0.52 g (0.80 mmol) of (**8b**) in 20 mL of ethyl acetate was refluxed with 2 mL of triethylamine. After washing with aqueous HCl, $NaHCO_3$, and water, the dried ($CaCl_2$) organic layer was evaporated . The residue was recrystallised from ethanol yielding 0.11 g(35%) of (**9**) m.p.157-8 °C. IR (Nujol) 3050, 1626, 1597, 1316, 1303, 1287, 1147, 1084, 1016, 979, 813, 656. ^{1}H-NMR ($CDCl_3$,200 MHz) ∂ 7.70 (d, 2H, J=8 Hz, Ar),7.33 (d, 2H, J=8 Hz, Ar), 6.83 (d, 1H, J=15 Hz, HC=), 6.28 (d, 1H, J=15 Hz, =CH), 2.45 (s, 3H, MeAr), 2.43-2.39 (m, 2H, CH_2). Mass spectrum,*m/e* (relative intensity) 390(M^+,17%), 234(22), 157(24), 139(96), 91(100), 79(97), 65(39), 45(40).

1,6-Bis(*p*-tolylsulphonyl)hexane(10). A mixture of 0.79 g (1.22 mmol) of bisadduct (**8b**) and 0.5 g(13.3 mmol) of sodium tetra-hydrideborate in 50 mL of DMSO was heated at 50-60 °C for 7 hours. The reaction misture was diluted with 150 mL of water and extracted with 3x75 mL of dichloromethane. The combined extracts were dried and the solvent was removed under reduced pressure. The residue was recrystallised from ethanol yielding 0.27 g (67%) of long crystals of (**10**) m.p. 156-7 °C. A similar reaction of the corresponding iodide (**8a**) yielded only 13% of (**10**). Anal. Calc. for $C_{20}H_{22}O_4S_2$: C,61.22; H,6.18; S,16.34; Found: C,61.14; H,6.73; S,16.22; IR (Nujol) 1598, 1399, 1315, 1304, 1281, 1204, 1142, 1088, 1046, 1021, 954, 819, 777, 724, 708, 666, 632 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) ∂ 7.76 (d, 2H,

J=8 Hz, Ar),7.33 (d, 2H, J=8 Hz, Ar),2.95-3.15(m, 2H, CH_2S),2.45 (s, 3H,MeAr),1.6-1.8 (m, 2H, CH_2),1.25-1.45 (m, 2H, CH_2); ^{13}C-NMR ($CDCl_3$) ∂ 14.67(Ar), 129.89(Ar), 136.08(Ar), 127.99(Ar), 56.05(CH_2S), 27.76(CH_2), 22.43(CH_2); Mass spectrum,*m/e* (relative intensity) 394(M^+,34%), 239(11), 225(7), 211(5), 157(100), 139(24), 91(77), 88(33), 65(23), 55(62), 41(40).

2-Iodo-3-*p*-tolylsulphonylpropyl methacrylate (12). A solution of 4.0 g (14.2 mmol) of tosyl iodide and 2.8 mL (20.7 mmol) of allyl methacrylate in 100 mL of CH_2Cl_2 was left under sunlight for 30 minutes. The colourless solution was evaporated under reduced pressure, yielding 6.24 g of a brown oil. The oil (1.0 g) was purified by radial chromatography (silica gel MercK 60 PF_{254}) yielding a mixture of (11) and (12). Recrystallised from tetrachloromethane yielded white crystals (0.18 g, m.p. 80-83 °C) of pure (12). ^{1}H-NMR ($CDCl_3$) ∂ 7.81 (d, 2H, J=8 Hz, Ar), 7.39 (d, 2H, J=8 Hz, Ar), 6.16 (d, 1H, J=0.5 Hz, $=C<^{H}$), 5.63 (q, 1H, J=1.5 Hz, $=C<_{H}$), 4.61-4.52 (m, 1H, CHI), 4.48-4.41 (m, 2H, OCH_2), 3.89-3.65 (m, 2H, CH_2Ts), 2.48 (s, 3H, MeAr), 1.96 (t, 3H, J=0.7 Hz, MeC=);^{13}C-NMR ($CDCl_3$) ∂ 166.11 (C=O), 145.46 (Ar), 135.92 (Ar), 135.53 (CO-C=), 130.19 (Ar), 128.11 (Ar), 126.51 ($=CH_2$), 67.63 (O-CH_2), 62.45 (CH_2-S), 21.85 (MeAr), 18.19 (Me), 13.96 (Cl).

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