Tetrahedron Vol. 46, No. 15, pp. 5285-5294, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

SULPHONYL RADICAL ADDITION TO NON-CONJUGATED DIENES REGIO- AND STEREOSELECTIVE CYCLIZATIONS

I. De Riggi, J.-M. Surzur and M.P. Bertrand*
Laboratoire de Chimie Organique B - Associé au CNRS n° 109

A. Archavlis
E.S.C.M

R. Faure
Laboratoire de Chimie Organique Physique - Associé au CNRS n°126

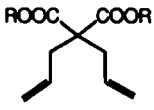
Faculté des Sciences St Jérôme - Avenue Escadrille Normandie-Niemen
13397 Marseille Cedex 13

(*Received in France* 26 *March* 1990)

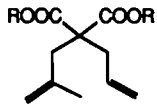
Abstract - Addition of TsBr to diallyl malonates and allyl methallyl malonates is described. These cyclization reactions exhibit high stereoselectivity and very high regioselectivity. The structure of the reaction products is elucidated using 2D NMR.

Resumé - Cet article décrit l'addition de TsBr sur des esters des acides diallyl malonique et allyl methallyl malonique. Ces réactions de cyclisation présentent respectivement une stéréosélectivité et une régiosélectivité trés élevées. Les analyses structurales des produits utilisant la RMN 2D, sont développées.

Free-radical addition of sulphonyl halides to unsaturated compounds is a valuable method for the synthesis of open-chain sulphones[1]. A few studies have been devoted to the application of this reaction to the preparation of alicyclic sulfones[2-5]. The recent report of the addition of tosyl chloride to 1,6-dienes, without any structural analysis of the stereoisomeric adducts[5], prompted us to describe our results in this field[6] in connection with our structural investigations. In a previous study[3], we reported the addition of tosyl halides to heterodienes. This paper deals with the regio- and the stereoselectivity of the addition of tosyl bromide to malonic derivatives: ethyl, methyl and t-butyl diallyl malonates (**1**, **2**, **3**), and ethyl and methyl allyl methallyl malonates (**4** and **5**).



1 (R = Et)
2 (R = Me)
3 (R = *t*-Bu)



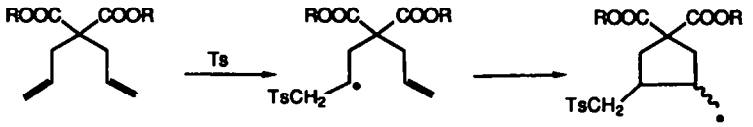
4 (R = Et)
5 (R = Me)

The reactions were performed either by irradiating 0,015M acetonitrile solutions of the diene in the presence of a stoichiometric amount of tosyl bromide[7] with a high-pressure mercury lamp, or in chlorobenzene under reflux. After completion, the solvent was evaporated and the products were isolated by liquid chromatography on silica gel, using ethyl acetate-petroleum ether as eluent.

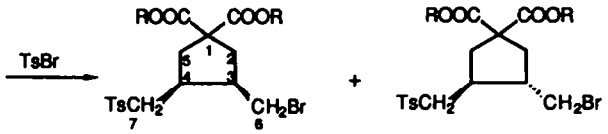
Results and Discussion

The reaction of the diallyl malonates **1**, **2** and **3** leads exclusively to cyclopentanic monoadducts **6**, **7** and

8 as mixtures of isomers (eq. 1).



eq. 1



1	20°C	**6a** (93)	**6b** (7)	85%
	135°C	(79)	(21)	85%
2	20°C	**7a** (90)	**7b** (10)	85%
	135°C	(81)	(21)	76%
3	20°C	**8a** (93)	**8b** (7)	87%

The isomer ratios were determined by ^{13}C NMR spectroscopy (cf experimental part), except for **8a** and **8b** the complete separation of which was achieved by liquid chromatography. Analysis of the γ gauche effect experienced by the two carbons bearing the tosyl and bromo groups respectively, allows an unambiguous distinction between the trans and cis adducts. The γ gauche interaction in the cis configuration contributes to a significant shielding of both methylene carbons. The assignment of the C_6 and C_7 resonances was made with **7a** as model, by selective irradiation of the CH_2Br protons and the superimposed signal of one of the protons of the CH_2Ts group. The results are listed in Table 1.

Table 1

^{13}C Chemical shifts in cis and trans isomers

Adduct	CH_2Ts	CH_2Br
6a	55.4	32.8
6b	60.0	35.1
7a	55.4	32.6
7b	59.8	35.0
8a	55.3	32.6
8b	60.3	35.1

The cis configuration in **6a** was confirmed by ^1H NMR. It was established by successive application of COSY long-range and NOESY experiments on the pure major adduct (resulting from **1**). The two-dimensional NOESY spectrum clearly exhibits a cross-peak between the two functionalised methylene groups. This interaction is not ambiguous since no correlation between H_6 and H_7 could be detected in the COSY long-range spectrum.

Unexpectedly, the major compound **7a** resulting from **2** did not show any NOE effect.

As expected the cis isomer predominates. Little change is observed in stereoselectivity by changing diethyl carboxylate **1** into dimethylcarboxylate **2** and even into di-t-butyl carboxylate **3**. At room temperature, the cis:trans ratio is 93:7 for **6**, 90:10 for **7** and 93:7 for **8**. This ratio was significantly modified by carrying out the addition of tosyl bromide to **1** and **2** under thermal initiation, at reflux in chlorobenzene (135 °C); the cis:trans ratio becomes 79:21 for **6** and 81:19 for **7**, respectively.

Table 2

Cis:trans ratio for substituted 5-hexenyl radical cyclizations

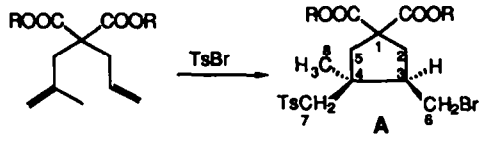
	R	T °C	cis : trans	ref
X=CH_2	Me	65	67:33	9
	Ph	80	0:100	10[a,b]
	COR	60-80	27:73	11[b]
	COOMe	60-80	55:45	11[b]
	COOtBu	60-80	47:53	11[b]
X=O	Rf	135	66:34	12
	CH_2Ts	20	81:19	3
	CH_2Ts	20	80:20	4[c]
	CH_2CCl_3	77	81:19	13
X=N-R'	CH_2Ts	20	75:25	3[c]
		-	83:17	14
	CH_2SCOMe	80	75:25	15
	CH_2CCl_3	77	86:14	13
X=C(COOR)$_2$	$CH=CH_2$	80	65:35	16[b,d]
	OTBS	80	40:60	17
	COOMe	80	82:18	17
	Ph	80	46:54	17[a,b]
	CH_2CCl_3	77	84:16	13
	CH_2SR	80	84:16	18
	CH_2Ts	20	93:7	this paper
	-	135	79:21	-
	-	100	84:16	5

a) These cyclizations are reversible. The extent of reversibility depends on the reaction conditions.
b) In these reactions, the six-membered ring product resulting from an *exo*-cyclization mode is also obtained.
c) These results refer to the addition of TsBr to the corresponding diene. Only the cis isomer is obtained with TsI but in lower yields.
d) The reversibility was shown to be low in that case.

As summarized in table 2 by a non exhaustive compilation of data, the cyclization of similar secondary radicals favors generally the cis 1,2- disubstituted five-membered ring resulting from an *exo*-cyclization mode[8]. This result is obtained when the cyclization process is irreversible. Starting from stabilized radicals,the major product can not only result from an *endo*-cyclization mode, but also the more stable trans five-membered ring product can be preferred over the cis one.This is the result of a reversible cyclization process[8]. The table shows that whenever comparative data are available, the selectivity in favor of the cis isomer is enhanced when $X=C(COOR)_2$ (cf. table 2).The high stereoselectivity observed with malonic derivatives fits well with the Beckwith stereoelectronic model of a chair-like transition state[8]. The presence of a bulky substituent, necessarily axial, on the carbon atom β to the radical center disfavors the pseudo-chair transition state, precursor of the trans cyclic isomer more than in the other cases, by introducing strong 1,3 diaxial interactions (fig.1). Molecular modeling taking into account as proposed by Houk[19] not only the chair-like transition state but also the boat-like form will be undertaken. Owing to the low temperature, the addition of TsBr reaches an exceptionnally high cis:trans ratio.

fig.1

As reported in eq. 2, the addition of tosyl bromide to allyl methallyl malonates **4** and **5** exhibits a very high regioselectivity. The overall yield is about 70-80%, and 91% of the purified isolated products result from the preferred attack of Ts on the terminus of the disubstituted double bond. Three products are formed and their ratio was determined by ^1H NMR on the crude mixture. The assignment is based on the relative integration of the signals corresponding to the C_8 methyl group. Unlike **A** and **B**, no pure sample of the minor compound, which exhibits a singlet at 1.09 ppm, could be isolated and its structure could not be deduced from the ^1H NMR in the presence of A or B.



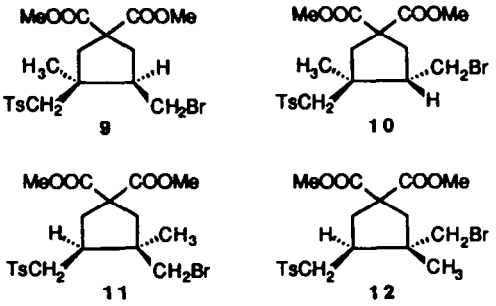
eq. 2

4	80%	52	39	9
5	70%	57	34	9

The structural determinations conducted on pure samples of the two major isomers require some comments. As exemplified by compound **5**, the problem was to find out, disregarding the less probable six-membered ring products[8,19], which of the four possible cyclopentanic adducts **9-12** were actually obtained.

The structures of the two isomers **A** and **B** were easily elucidated by the application of both one and two-

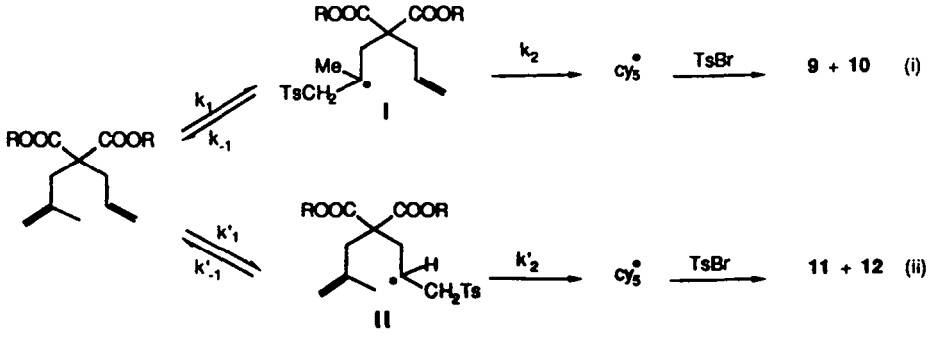
dimensional NMR experiments. The 2D ^{1}H-^{13}C heteronuclear chemical shift correlations establish the carbon-proton connectivities and therefore identify the location of each pair of methylene protons. In particular, H_{7a} and H_{7b} could be assigned unambiguously, owing to the deshielding effect of the tosyl group on the ^{13}C chemical shift (as reported above for **7a** and **7b**). The J ^{1}H-^{1}H splitting pattern (cf. experimental part), unequivocally excludes structures **11** and **12**, as well as six-membered ring skeletons.



Once the question of the regioselectivity was solved, it was necessary to determine which of compounds **9** and **10** was the major isomer. The answer was given by the chemical shift value of the carbon of the additional methyl group (C_8). Owing to the γ gauche effect, it should be higher in **9** than in **10**. The contour plot of the heteronuclear correlation diagram identifies unambiguously the values for the CH_3 groups bonded to the aromatic ring. Consequently, the respective chemical shifts for C_8 were 25.2 ppm in **A** and 19.9 ppm in **B** and therefore, **A** corresponds to **9** and **B** to **10**.

The high regioselectivity of the addition of sulphonyl radicals towards the more substituted double bond leading to products resulting from **I** rather than from **II** could be ascribed to the electrophilic nature of this radical[20].We tentatively suggest that a more general kinetic scheme needs to be considered (Scheme 1), although we have no quantitative knowledge of the individual rate constants.

Scheme 1



Owing to the reversibility of the addition step[21], the difference between the rate constants k_2 and k'_2 of

the two possible cyclization steps is of prime importance. It is well known from the rate constants for cyclization of analogous alkenyl radicals, that a methyl group on the internal position of the double bond (like in **II** compared to **I**) decreases dramatically the cyclization rate towards the five-membered ring[8,22].The formation of **9** + **10** in high yield could be ascribed to $k_2 > k'_2$ and to $k'_2 < k'_{-1}$. The same analysis could rationalize the results of the free- radical addition of TsCl to ethyl allyl 3-methyl-2-butenyl malonate where products resulting from the initial addition to the less substituted double bond are obtained exclusively and in high yield[5].

In conclusion, these results demonstrate that the free-radical reaction of sulphonyl bromide with 1,6-dienes proceeding by a regioselective initial addition step and a stereoselective subsequent cyclization step, is a valuable method for the synthesis of polysubstituted cyclic sulphones. We are further investigating the scope of this reaction on suitable models.

Experimental Section

Melting points are uncorrected. Column chromatography was performed on silicagel 60 (Merck 7734). Sulphonyl bromide was prepared according to a procedure previously described for sulphonyl iodide[23] and was dried under vacuum before use. Dienic starting materials were obtained by dialkylation of the corresponding malonic esters (**1**, **2**, **3**) or by alkylation of monoallyl malonic acid esters (**4**, **5**) according to known procedures[24].

NMR Experiments.

The 1D NMR spectra were recorded on Bruker AC-100 and AM-200 spectrometers. Two-dimensional ^{13}C and ^{1}H measurements were carried out using $CDCl_3$ as solvent and tetramethylsilane as internal standard. ^{1}H coupling constant were extracted from the resolution-enhanced ^{1}H spectrum using the gaussian multiplication technique[25].

Resonance multiplicities for ^{13}C were established via the acquisition of DEPT[26] spectra obtained for proton pulse $P_\Theta = 90°$ (CH only) and $P_\Theta = 135°$ (CH and CH_3 differentiated from CH_2). Typical parameters for the DEPT sequence are as follows (AM-200 spectrometer): width of a ^{13}C 90° pulse, 15μs; width of a ^{1}H 90° pulse, 29μs and ($2J^{-1}$) delay, 3.7 ms.

The homonuclear ^{1}H-^{1}H chemical shift correlated two-dimensional diagrams optimized for the observation of long-range couplings (COSY LR in the operating Bruker software) were obtained using the COSY LR-90 pulse sequence[27]. The spectral widths were F_2 = 1000 Hz and $F_1 = \pm$ 500 Hz allowing a digital resolution of 1.95 Hz per point. These spectra were collected as 1024 x 512 blocks of data and were processed using sinusoidal multiplication in each dimension followed by symmetrization of the final data matrix. Other parameters were as follows: number of increments in t_1, 256; scans, 64; phase cycling, 0.08 s and relaxation delay, 1 s. The homonuclear shift correlation experiments which are mediated by dipolar cross relaxation[28] (NOESY) were applied using the same parameters and the mixing delay was 1 s with ± 5% random variation.

Heteronuclear two-dimensional ^{1}H-^{13}C chemical shift correlation experiments were obtained with proton decoupling in the F_1 dimension[29] (XHCORRD). The spectra were acquired with 4K x 256 data points and a data acquisition of 160 x 128 increments in t_1 and a zero filling in the F_1 dimension. Spectral widths of 5000 and ± 500 Hz were employed in the F_2 (^{13}C) and F_1 (^{1}H) domains respectively. Data were processed using unshifted

sine bell functions for weighting in both dimensions, this provided a digital resolution of 2.44 Hz in F_2 and 3.9 Hz in F_1. The refocusing delay was 2 ms; the mixing delay, 4 ms; the relaxation delay, 2 s and sixteen phase cycling were employed.

The quantitative determination of the diastereoisomeric excess was performed using the peak areas of the ^{13}C NMR signals since ^1H NMR spectroscopy yielded insufficient separation of the resonances. Carbons 7,3,4 and 6 which are well resolved and assigned unambiguously, were used to quantify the diastereoisomers mixture. From the literature data[30], it seems that samples where relaxation times and NOE are likely to be very similar for the nuclei being compared, quantitative results may be obtained without the addition of paramagnetic materials, using only a long relaxation delay.

General procedure for the photoinitiated addition of TsBr.

In a typical experiment, a stirred solution of 0.57g (2.38 mmole) of ethyl diallyl malonate and 0.56g (2.38 mmole) of tosyl bromide was irradiated during 14h. The reaction vessel and the high pressure Hanau Q81 mercury lamp (fitted with a pyrex jacket) were immersed in a water bath whose temperature was maintained by circulation of water. After solvent evaporation, the residue was chromatographed on silica gel, using petroleum ether : ethyl acetate mixtures of gradually increased polarity (15 to 40%). 950 mg (84%) of a mixture of the adducts **6a** and **6b**, whose ratio (93:7) was determined by ^{13}C NMR, were isolated. The pure major isomer **6a** was obtained from the mixture by recrystallization from ethanol. Yields refer to converted diene (0-10% was recovered unchanged).

General procedure for the thermally intiated addition of TsBr.

In a typical experiment, a solution of 0.5g (2.36 mmole) of methyl diallyl malonate and 0.55g (2.36 mmole) of tosyl bromide was stirred at reflux during 24h. After evaporation of the solvent, the residue was chromatographed on silica gel as described above. After recovery of 50mg of a mixture of starting materials, 800mg of a mixture of adducts **7a** and **7b** were isolated (76%). Pure **7a** was isolated by crystallization from ethanol.

Ethyl 4-bromomethyl-3-tosylmethyl-cyclopentane-1,1-dicarboxylate (6a and 6b).

6a (cis isomer): ^1H NMR ($CDCl_3$): 7.85 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 4.20 and 4.19 (two superimposed q, J = 7.1 Hz, 4H), 3.30 (d, J = 6.7 Hz, 2H) (CH_2Br), 3.16 (superimposed AB part of an ABX, J_{AB} = 13.8 Hz, J_{AX} = 8 Hz, J_{BX} = 4.8 Hz, 2H) (CH_2Ts), 2.5-2.3 (m, 5H), 2.46 (superimposed s, 3H), 2.23 (dd, J = 13.8 and 6.3 Hz, 1H), 1.25 and 1.24 (two superimposed t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): 172 (C=O), 171.7 (C=O), 144.9 (=CSO_2), 136.3 (=CCH_3), 130.0 (=CH), 128.0 (=CH), 61.7 (CH_2O), 61.6 (CH_2O), 58.4 (C_1), 55.4 (C_7), 44.1 (C_3), 37.9 (C_2, C_5), 36.5 (C_4), 32.8 (C_6), 21.61 (CH_3C=), 14.0 (2xCH_3CH_2O).

Anal. Calcd for $C_{20}H_{27}O_6SBr$: C, 50.53; H, 5.72; S, 6.74. Found: C, 50.68; H, 5.74; S, 6.8.

6b (trans isomer): ^1H NMR: the main difference, deduced from the mixture spectrum, originates from H_{6a} signal appearing at 3.43 ppm (dd, J = 10.8 and 4.2 Hz). ^{13}C NMR ($CDCl_3$): no difference is noticed for the chemical shifts of the carbons of the tosyl and ethyl groups. 171.4 (C=O), 60.0 (C_7), 58.5 (C_1), 46.1 (C_3),

39.8 (C_2*) (these assignments might be reversed), 38.4 (C_5*), 37.6 (C_4), 35.1 (C_6).

Methyl 4-bromomethyl-3-tosylmethyl-cyclopentane-1,1-dicarboxylate (7a and 7b).
7a (cis isomer): Melting point: 82°C. ^{1}H NMR ($CDCl_3$): 7.79 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.74 and 3.73 (two s, 6H), 3.29 (d, J = 6.6 Hz, 2H) (CH_2Br), 3.24 (superimposed AB part of an ABX, J_{AB} = 13.9 Hz, J_{AX} = 8.1 Hz, J_{BX} = 4.9 Hz, 2H) (CH_2Ts), 2.7-2.48 (m, 4H), 2.46 (superimposed s, 3H), 2.24 (dd, J = 13.9 and 6.5 Hz, 1H), 2.42 (dd, J = 13.9 and 6.1 Hz). ^{13}C NMR ($CDCl_3$): 172.3 (C=O), 172.1 (C=O), 144.9 (=CSO_2), 136.2 (=CCH_3), 130.0 (=CH), 127.9 (=CH), 58.2 (C_1), 55.4 (C_7), 52.9 (2xCH_3O), 44.0 (C_3), 38.0 (C_5, C_2), 36.4 (C_4), 32.6 (C_6), 21.5 (CH_3).
Anal. Calcd for $C_{18}H_{23}O_6SBr$: C, 48.33; H, 5.18; S, 7.17. Found: C, 48.22; H, 5.24; S, 7.1.

7b (trans isomer): ^{1}H NMR: as mentionned above for **6b**, the spectrum of a mixture enriched in **7b** presents signals at 3.45 (dd, J = 10.4 and 4.1 Hz, 1H) (H_{6a}), 3.37-3.27 (unresolved m, 2H) (H_{6b} and H_{7a}), 3.11 (dd, J = 14.0 and 8.9 Hz) (H_{7b}). ^{13}C NMR: the carbons of the tosyl and methoxyl groups show identical chemical shifts in **7a** and **7b**. 171.8 (C=O), 59.8 5 (C_7), 58.2 (C_1), 45.9 (C_3), 39.8 (C_2*), 38.5 (C_5*), 37.6 (C_4), 35.0 (C_6).

***t*-Butyl 4-bromomethyl-3-tosylmethyl-cyclopentane-1,1-dicarboxylate (8a and 8b).**
^{1}H spectra are identical to those of **6** and **7**. The protons of the tBu group give rise to singlets at 1,44 and 1,46 ppm in **8a** and 1,43 and 1,44 ppm in **8b**.
8a (cis isomer): ^{13}C NMR: 171.0 (C=O), 170.7 (C=O), 144.6 (=CSO_2), 136.1 (=CCH_3), 129.8 (=CH), 127.8 (=CH), 81.5 (C-O), 81.2 (C-O), 59.5 (C_1), 55.3 (C_7), 44.0 (C_3), 37.5 (C_2, C_5), 36.3 (C_4), 32.6 (C_6), 27.5 (CH_3), 21.4 (CH_3C=).

8b (trans isomer): ^{13}C NMR: 170.5 (C=O), 144.7 (=CSO_2), 136.3 (=CCH_3), 129.8 (=CH), 127.9 (=CH), 81.4 (C-O), 60.3 (C_7), 60.0 (C_1), 46.2 (C_3), 39.6 (C_2*), 38.2 (C_5*), 37.6 (C_4), 35.1 (C_6), 27.7 (CH_3), 21.6 (CH_3C=).

Methyl 4-bromomethyl-3-methyl-3-tosylmethyl-cyclopentane-1,1-dicarboxylate (9 and 10).
9 (cis isomer): Melting point (ethanol): 105°C. ^{1}H NMR: 7.77 (d, J = 8.2 Hz, 2H) (=$CHCSO_2$), 7.36 (d, J = 8.2 Hz, 2H) (=$CHCCH_3$), 3.80 and 3.76 (two s, 6H) (CH_3O), 3.42 (dd, J = 9.9 and 4.4 Hz, 1H) (H_{6a}), 3.27 (d, J = 14.8 Hz, 1H) (H_{5a}), 3.18 (d, J = 13.6 Hz, 1H) (H_{7a}), 3.06 (t, J = 9.9 Hz, 1H) (H_{6b}), 2.77 (dd, J = 13.6 and 1.3 Hz, 1H) (H_{7b}), 2.59 (dd, J = 14.3 and 7 Hz, 1H) (H_{2a}), 2.46 (s, 3H) (CH_3C=), 2.45 (dd, J = 14.8 and 1.4 Hz, 1H) (H_{5b}), 2.37 (dd, J = 14.3 and 10.9 Hz, 1H) (H_{2b}), 2.14 (m, 1H) (H_3), 1.57 (s, 3H) (CH_3). ^{13}C NMR: 172.6 (C=O), 172.1 (C=O), 144.3 (=CSO_2), 138.4 (=CCH_3), 129.6 (=CH), 127.2 (=CH), 58.5 (C_7), 56.1 (C_1), 53.8 (C_3), 52.8 (CH_3O), 52.7 (CH_3O), 45.3 (C_4), 44.1 (C_5), 37.6 (C_2) 31.1 (C_6), 25.2 (C_8), 21.2 (CH_3C=).
Anal. Calcd for $C_{19}H_{25}O_6SBr$: C, 49.46; H, 5.46; S, 6.95. Found: C, 49.15; H, 5.49; S, 6.8.

10 (trans isomer): Melting point (ethanol): 135°C. ^{1}H NMR: 7.80 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz,

2H), 3.74 (s, 6H), 3.43 (dd, J = 10.2 and 4.9 Hz, 1H) (H_{6a}), 3.42 (d, J = 13.9 Hz, 1H) (H_{7a}), 3.22 (dd, J = 10.2 and 8.7 Hz, 1H) (H_{6b}), 3.10 (d, J = 13.9 Hz, 1H) (H_{7b}), 2.84 (d, J = 14.7 Hz, 1H) (H_{5a}), 2.62 (unresolved signal due to second order effect, 1H) (H_{2a}), 2.60 (d, J = 14.7 Hz, 1H) (H_{5b}), 2.46 (s, 3H) (CH_3C=), 2.25 (m, 2H) (H_{2b}-H_3), 1.20 (s, 3H) (CH_3). ^{13}C NMR: 172.7 (C=O), 172.1 (C=O), 144.7 (=CSO_2), 138.4 (=CCH_3), 130.0 (=CH), 127.6 (=CH), 66.1 (C_7), 57.1 (C_1), 53.1 (CH_3O), 53.0 (CH_3O), 51.2 (C_3), 47.0 (C_5), 44.4 (C_4), 37.8 (C_2), 31.4 (C_6), 21.6 (CH_3C=), 19.9 (C_8).
Anal. Calcd for $C_{19}H_{25}O_6SBr$: C, 49.46; H, 5.46; S, 6.95. Found: C, 49.46; H, 5.40; S, 7.00.

Ethyl 4-bromomethyl-3-methyl-3-tosylmethyl-cyclopentane-1,1-dicarboxylate (9' and 10').
9' (cis isomer): ^1H NMR: 7.78 (d, J = 8.2 Hz, 2H) (=$CHCSO_2$), 7.36 (d, J = 8.2 Hz, 2H) (=$CHCCH_3$),4.24 (m (instead of two superimposed quartets, the complex splitting pattern seems to indicate a hindered rotation and the magnetic non-equivalence of the protons in a methylene group), 4H) (CH_2O), 3.44 (dd, J = 9.9 and 4.2 Hz, 1H) (H_{6a}), 3.25 (d, J = 14.8 Hz, 1H) (H_{5a}), 3.20 (superimposed d, J = 13.6 Hz, 1H) (H_{7a}), 3.07 (t, J = 9.9 Hz, 1H) (H_{6b}), 2.80 (d, J = 13.6 Hz, 1H) (H_{7b}), 2.62 (dd, J = 13.8 and 6.7 Hz, 1H) (H_{2a}), 2.45 (s, 3H) (CH_3C=), 2.10-2.50 (m, 3H) (H_{5b}, H_{2b}, H_3), 1.49 (s, 3H) (CH_3), 1.27 and 1.26 (two superimposed t, J = 7.1 Hz, 6H) (CH_3CH_2). ^{13}C NMR: 172.8 (C=O), 172.2 (C=O), 144.7 (=CSO_2), 136.9 (=CCH_3), 130.1 (=CH), 127.7 (=CH), 62.1 (CH_2O), 61.9 (CH_2O), 59.2 (C_7), 56.8 (C_1), 54.2 (C_3), 45.8 (C_4), 44.6 (C_5), 38.1 (C_2) 31.6 (C_6), 25.7 (C_8), 21.8 (CH_3C=), 14.1 (CH_3CH_2).
Anal. Calcd for $C_{21}H_{29}O_6SBr$: C, 51.54; H, 5.97; S, 6.55. Found: C, 51.55; H, 5.96; S, 6.4.

10' (trans isomer): Melting point (ethanol): 113 °C. ^1H NMR: 7.80 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 4.19 and 4.18 (two superimposed q, J = 7 Hz, 4H), 3.42 (dd, J = 10.2 and Hz, 1H) (H_{6a}), 3.41 (d, J = 13.9 Hz, 1H) (H_{7a}), 3.21 (dd, J = 10.2 and 8.7 Hz, 1H) (H_{6b}), 3.10 (d, J = 13.9 Hz, 1H) (H_{7b}), 2.83 (d, J = 14.7 Hz, 1H) (H_{5a}), 2.62 (unresolved multiplet, 1H) (H_{2a}), 2.54 (d, J = 14.7 Hz, 1H) (H_{5b}), 2.45 (s, 3H) (CH_3C=), 2.23 (m, 2H) (H_{2b}-H_3), 1.20 (s, 3H) (CH_3) 1.25 and 1.24 (two superimposed t, J = 7 Hz, 6H) (CH_3CH_2). ^{13}C NMR: 172.5 (C=O), 171.9 (C=O), 144.9 (=CSO_2), 138.7 (=CCH_3), 130.2 (=CH), 127.8 (=CH), 66.4 (C_7), 62.1 (CH_2O), 62.0 (CH_2O), 57.5 (C_1), 51.5 (C_3), 47.1 (C_5), 44.6 (C_4), 37.9 (C_2), 31.7 (C_6), 21.6 (CH_3C=), 20.2 (C_8), 14.2 (CH_3CH_2).
Anal. Calcd for $C_{21}H_{29}O_6SBr$: C, 51.54; H, 5.97; S, 6.55. Found: C, 51.56; H, 6.03; S, 6.7.

References and Notes

1 - a) Schank, K. in " The Chemistry of Sulphones and Sulphoxides", Ed. Patai, S. and Rappoport, Z. and Stirling, C., 1988, John Wiley and Sons, p. 165 and ref. therein. b) Chatgilialoglu, C. *ibid*, p. 1089 and ref. therein.
2 - a) Cristol, S.J.; Harrington, J.K.; Singer, M.S. J. *Am. Chem. Soc.* **1966**, *88*, 1529. b) Gubernatov, V.K.; Kogai, B.E.; Sokolenko, V.A. *Izv. Akad. Nauk SSR, Ser. Khim.* **1983**, 1874: *Chem. Abstr.* **1983**, *99*, 194486. c) Gubernatov, V.K.; Kogai, B.E.; Korniets, E.D.; Sokolenko, V.A. *Zh. Org. Khim.* **1983**, *19*, 2209: *Chem. Abstr.* **1984**, *100*, 209277.
3 - De Riggi, I.; Surzur, J.-M.; Bertrand, M.P. *Tetrahedron*, **1988**, *44*, 7119. Yields reported therein have been improved by lengthening the irradiation time (16 - 20h); this brings them up to 70% for the addition of TsBr to diallylether and up to 74% for the addition of TsBr to N-diallyltosylamide.
4 - a) Serra, A.C.; Da Silva Corrêa, C.M.M. *J. Chem. Research (S)* **1989**,85. b) *ibid, J; Chem. Research (M)*

1989, 801.
5 - Chuang, C.-P.; Ngoi, T.H. *Tetrahedron Lett.* **1989**, *30*, 6369.
6 - These results have first been reported in a communication to the French Chemical Society in Marseille, (April 1989).
7 - The external irradiations were performed in a pyrex vessel. All the described experiments were first conducted in the presence of a catalytic amount of AIBN. Further experiments conducted without the relay of an initiator were shown to give similar results.
8 - a) Beckwith, A.L. *Tetrahedron* **1981**, *37(18)*, 3073. b) Surzur, J.-M.in *"Reactive Intermediates"*, Ed. Abramovitch, A., **1981**, Plenum Press, New-York, *Vol.2*, Chapt. 3.
9 - Beckwith , A.L.; Blair, I.A.; Phillipou, G. *Tetrahedron Lett.* **1974**, *26*, 2251.
10 - Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6064.
11- Curran, D.P.; Chang, C.T. *J. Org. Chem.* **1989**, *54*, 3140.
12- Brace, N.O. *J. Org. Chem.* **1979**, *44*, 213.
13- Grigg, R.; Devlin, J.; Ramasubbu, A.; Scott, R.M.; Stevenson, P. *J. Chem. Soc., Perkin Trans I* **1987**, *7*, 1515.
14 - Hawthorne, D.G.; Johns, S.R.; Willing, R.I. *Aust. J. Chem.* **1976**, *29*, 315.
15- Padwa, A.; Nimmesgern, H.; Wong, G.S.K. *J.Org. Chem.* **1985**, *50*, 5620.
16- Stork, G.; Reynolds, M.E. *J.Am. Chem. Soc.* **1988**, *110*, 6911.
17- Curran, D.P.; Kim, D.; Liu, H.T.; Shen, W. *J. Am. Chem. Soc.* **1988**, *110*, 5900.
18- Kuehne, M.E.; Damon, R.E. *J. Org. Chem.* **1977**, *42*, 1825.
19-Spellmeyer, D.C.; Houk, K.N. *J. Org. Chem.* **1987**, *52*, 959.
20- a) Da Silva Corrêa, C.M.M.; Waters, W.A. *J. Chem. Soc., Perkin Trans II* **1972**, *2*,1575. b) Takahara, Y.; Iino, M.; Matsuda, M. *Bull. Chem. Soc. Japan* **1976**, *49*, 2268.
21- a) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**,4962. b) Sinneich, J.; Asscher, M. *J. Chem. Soc., Perkin Trans I* **1972**, 1543. c) Boothe, T. E.; Greene, Jr., J.L.; Shevlin, P.B. *J. Org. Chem.* **1980**, *45*, 794. d) Lin, P.; Whitham, G.H. *J. Chem. Soc., Chem. Commun.* **1983**, 1102. e) Smith, T.A.K.; Whitham, G.H. *ibid*, **1985**, 897.
22- Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**,*94*, 6059.
23- Truce, W.E.; Wolf, G.C. *J. Org. Chem.* **1971**, *36*, 1727. A solution of bromine in EtOH is added dropwise to an aquous solution of sodium paratoluene sulfinate (yield: 60-70%).
24- Mook Jr., R.; Sher, P.M. in *"Organic Syntheses"*, Heathcock, C.H., Ed., **1987**, *Vol. 66*, 75.
25- Ferrige, A.G.; Lindon, J.C. *J. Magn. Reson.* **1978**, *31*,337.
26- Doddrell, D.M.; Pegg, D.T.; Bendall, M.R. *ibid.* **1982**, *48*, 323.
27- a) Bax, A.; Freeman, R. *ibid.* **1981**, *44*, 542. b) Benn, R.; Günther, H. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 390.
28- a) Meir, B.H.; Ernst, R.R. *J. Am. Chem. Soc.* **1979**, *101*, 6441. b) Jeener, J.; Meir, B.H.; Bachmann, P.; Ernst, R.R. *J. Chem. Phys.* **1979**, *71*, 4546.
29- a) Bax, A. *J.Magn. Reson.* **1983**, *53*, 517. b) Rutar, V.J. *ibid.* **1984**, *58*, 306.
30- a) O'Neill, I.K.; Pringuer, M.A. *Org. Magn. Reson.*, **1974**, *6*, 398. b) Chiang, H.C.; Lin, L.J. *ibid.* **1979**, *12*, 260. c) Reisse, J.; Zimmermann, D.; Charles, J.-P.; Christol, M.; Solladie, G. *Bull. Soc. Chim. Fr.* **1972**, 2764.