The stereochemistry of addition of allyl sulfone carbanions to aldehydes. Formation of dihydrofurans ¹

Alfred Hassner,* Avital Laxer, and Eugene Ghera
Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel
E-mail: hassna@mail.biu.ac.il

This paper is dedicated in friendship and with best wishes to Prof. Albert Padwa on the occasion of his 65th birthday
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Abstract
The reaction of the mono-anion of the bromoallyl sulfone ¹ with aldehydes ² was examined with the aim of obtaining selectively substituted tetrahydrofurans. At –100°C syn- and anti- open chain adducts ³ and ⁴ were isolated together with a low yield of 4-methylene-2,3-disubstituted tetrahydrofuran ⁵. In the presence of HMPA or at higher temperature the reaction led to formation of 2,5-dihydrofurans ⁶. The stereochemical results are consistent with initial addition of ¹ to the aldehyde involving Li ion chelation.

Keywords: Dihydrofurans, Michael additions, allyl sulfones, Li chelation

Introduction
Recently we have shown ²,³ that 2-(bromomethyl)-3-phenylsulfonyl-1-propene ¹ reacts with one molar equivalent of LDA to generate a lithiated α-allylsulfone carbanion that is stable at low temperature and undergoes regioselective and stereoselective additions via the α-carbon to Michael acceptors such as unsaturated esters, ketones, sulfones and nitro compounds, followed by cyclization to methylene-cyclopentenes. For instance, in the case of unsaturated esters, the primary Michael adduct was not even isolable at –78°C and the incipient carbanion immediately underwent intramolecular reaction with the allylic bromide to afford stereoselectively substituted methylenecyclopentane derivatives (eq. 1).² The high stereoselectivity in the product can be rationalized on the basis of Li-ion chelation by the sulfone and the ester function during addition.

The addition of lithiated ¹ to the C=N of sulfinimines proceeded less stereoselectively and led with double bond rearrangement to 2-arylpyrrolines.³
In view of general interest in formation of stereoselectively substituted tetrahydrofurans, such as the naturally occurring polyether antibiotics, we investigated the reaction of 1 with aldehydes as a potential entry into substituted tetrahydrofurans. We report here our findings, using the mono-lithio derivative of the bromoallyl sulfone 1 and of the hydroxyallylsulfone 8 in reactions with aldehydes 2.

Results and Discussion

The bromoallylsulfone 1 was deprotonated using 1.1 equiv. of LDA in THF at −100°C. The monolithio derivative thus generated was treated with p-nitrobenzaldehyde 2d at the same temperature and quenched after 30 min with HOAc to give a mixture of two open chain syn- and anti- isomers, 3 and 4, as well as the trans- 2,3-disubstituted-4-methylenetetrahydrofuran 5 (see eq. 2 and Table 1, entry 2).

The syn- and anti- isomers 3 and 4 were separated by flash-column chromatography and their structures in the preferred conformation were assigned as 3A and 4A, respectively, on the basis of NMR data. Similarly, the structure assignment of 5 is based on NMR (see discussion below). Addition of LiBr to the reaction mixture did not alter the results: however, addition of a solvating agent (TMEDA or especially HMPA) at −100°C did change the ratio of products and led to
isolation of the dihydrofuran 6d, with the syn isomer 3 remaining unchanged (see Table 1). In two cases, a Michael adduct of the anion derived from product 5 to the aldehyde 2d, was isolated in ca. 5% yield.

![Chemical structures](image)

Reaction at higher temperature (-40ºC) for a longer period of time (3 h) in the absence of HMPA afforded the syn- isomer 3 together with rearranged dihydrofuran 6d. When the monolithio derivative of 1 was treated with aldehyde 2d followed by HMPA in excess, and allowed to react at –40ºC for 3 h, the only product isolated was the dihydrofuran 6d (see Table 1).

### Table 1. Products 3–6 from reaction of 1 with 1.1 eq. of LDA followed by p-nitrobenzaldehyde, 2d

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>3, Yield (%)</th>
<th>4, Yield (%)</th>
<th>5, Yield (%)</th>
<th>6, Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5h, -100ºC</td>
<td>51</td>
<td>22</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.5h, -100ºC, LiBr</td>
<td>51</td>
<td>22</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>3a</td>
<td>1h, -100ºC, TMEDA</td>
<td>50</td>
<td>8</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>4a</td>
<td>1h, -100ºC, HMPA</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>3h, -40ºC</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>3h, -40ºC, HMPA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>48</td>
</tr>
</tbody>
</table>

In this manner, several aliphatic and aromatic aldehydes 2a–d were converted to the dihydrofurans 6a–d by means of the monolithio- derivative of 1 at –40ºC in the presence of HMPA, in good yields (see Table 2).

### Table 2. Dihydrofurans 6 from reaction of 1 with LDA and aldehydes 2 (a–d) in the presence of HMPA at –40ºC

<table>
<thead>
<tr>
<th></th>
<th>R</th>
<th>6, Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>CH₃(CH₂)₂⁻</td>
<td>63</td>
</tr>
<tr>
<td>b</td>
<td>CH₃(CH₂)₄⁻</td>
<td>52</td>
</tr>
<tr>
<td>c</td>
<td>p-Tolyl⁻</td>
<td>85</td>
</tr>
<tr>
<td>d</td>
<td>p-Nitrophenyl⁻</td>
<td>48</td>
</tr>
</tbody>
</table>
While this work was in progress, Najera et al.\textsuperscript{6} reported the formation of the dianion of the chloro analog of 1 using 2 equiv. of BuLi and DMPU and its reaction with alkyl halides and aldehydes (eq. 3). With alkyl halides, dialkylation took place. Allowing the reaction with aldehydes to proceed to room temperature, led to dihydrofuran analogs of 6, while the reaction with propanal and quenching at \(-40^\circ\text{C}\) gave a mixture of 6 and open-chain diastereomeric adducts. However, no separation of the latter, or their stereochemical elucidation, was reported.

\begin{equation}
\text{eq. 3} \quad \text{ArSO}_2\text{Cl} \xrightarrow{2 \text{BuLi}} \text{ArSO}_2\text{Li} \xrightarrow{\text{R'-CHO}} \text{ArSO}_2\text{R} \quad \text{O}
\end{equation}

Our stereochemical results are best explained via the “cyclic model” in which the lithio allylsulfone carbanion reacts by an $\alpha$-carbon attack on the aldehyde leading to a chelated intermediate. As can be seen, the syn-chelated structure 3B (likely as a chair conformer of a 6-membered ring with two equatorial groups) should be favored over syn- 3C or over anti- 4A\textsuperscript{7} because of gauche interactions; this explains why the syn product predominates.
When chelation of the Li cation with sulfone- and alcohol- oxygens is disrupted, as in the presence of HMPA, rotation can occur to 3C and 4B, respectively,\(^7\) conformers needed for subsequent cyclization. In this case, it is the \textit{anti-} isomer in its anionic form (4B or 4C) which is expected to ring-close to a tetrahydrofuran 5, while steric hindrance inherent in vicinally \textit{cis-} disubstituted five-membered rings should raise the transition state energy for the cyclization of \textit{syn-} 3C. Indeed, only cyclization of the \textit{anti-} isomer to the \textit{trans-} tetrahydrofuran 5 was observed at \(-100^\circ\text{C}\) (Table 1, entry 4). At higher temperature and in the presence of HMPA and base, ring closure of both diastereomers took place followed by isomerisation to the dihydrofuran 6, as well as side reactions. The above series of events is consistent with the products which we had observed in the reaction of 1 with \(\omega\)-nitrostyrene, in which the \textit{anti-} adduct ring-closed more readily (to the \textit{trans-} substituted cyclopentane) than did the \textit{syn-} isomer.\(^3\)\(^b\)

It was hoped that chelation to the hydroxyallylsulfone 8 might lead to higher stereoselectivity during the addition to the carbonyl group by complexation, as shown in 9. In fact, the hydroxyallylsulfone 8 had been shown to add regio- and stereoselectively to nitro-olefins.\(^8\) Hence, we also examined the condensation of the Li derivative of 8 with hexanal 2b. In this case, however, two diastereomers 10 (\textit{syn-}) and 11 (\textit{anti-}) were formed in essentially equal amounts and addition of TMEDA did not change the results. Apparently, in this system chelation of the Li cation from the aldehyde to the sulfone or the hydroxy group are either not important, or more likely, equal.

\[
\begin{align*}
\text{eq. 4} & \quad \text{PhSO}_2\text{H} \quad \text{OH} & \quad \text{PhSO}_2\text{H} \quad \text{OH} \\
8 & \quad \text{C}_3\text{H}_{11} & \quad \text{C}_3\text{H}_{11} + \\
2b & \quad \text{OH} & \quad \text{OH} \\
10 \text{syn} & \quad \text{11} \text{anti}
\end{align*}
\]

**Structure assignment**

The configurational assignment of 3A as the \textit{syn-} isomer is based on a value of 9 Hz for the coupling constant between H\(_a\) and H\(_b\) indicating an \textit{anti-} relationship. In the second isomer 4A the corresponding coupling constant is 2.5 Hz, consistent with a \textit{gauche} orientation of H\(_a\) and H\(_b\). In both isomers the hydroxylic proton exhibits a doublet with coupling to H\(_b\) of 2 Hz. This phenomenon is known in cases where the exchange rate of the hydroxylic proton is very low and may be due to hydrogen bonding. The determination of configuration of the \textit{trans-} substituted tetrahydrofuran 5 is also based on a 4 Hz coupling between H\(_a\) and H\(_b\). Although configurational assignment in 5-membered rings based on NMR should be made with caution in cyclopentanes that are rather flat, \textit{trans-} vicinal hydrogens usually show a small coupling constant of 2–4 Hz (dihedral angle near 120º) while \textit{cis-} vicinal hydrogens exhibit a larger coupling constant of 8–11 Hz (dihedral angle closer to 0º). In the case of 5 the assumption that the ring is rather flat is well
founded since (a) there is an sp^2 hybridized center in the ring, (b) the 5-membered ring contains an oxygen atom, (c) each of the vinylic protons shows three similar allylic couplings (with H_a, H_c, H_d). This is consistent with having C_3, C_4, C_5 in nearly the same plane. More convincing is the NOE (2%) observed in 5 between H_a and the ortho-hydrogens of the cis-p-nitrophenyl ring, as well as between H_a and H_d and between H_b and H_c.

In conclusion, the lithio allylsulfone carbanion derived from 1 added stereoselectively to aldehydes to produce preferentially the syn-adduct at low temperature (–100ºC). This is best explained by a chelated intermediate 3B, while at higher temperature and in the presence of HMPA, ring-closure and finally isomerisation to the dihydrofuran 6 took place. There was no stereochemical preference in the addition of hydroxysulfone 8 to aldehyde 2b.

**Experimental Section**

General anhydrous experimental techniques and analytical measurements were as previously described.8

**General procedure for the reaction of 1 with p-nitrobenzaldehyde (2d); Formation of 3–7**

To a stirred solution of LDA (prepared from 0.14 mL (1 mmol) of diisopropylamine and 0.64 mL of n-BuLi (0.92 mmol, 1.475 N in hexane) in 4 mL of THF) was added dropwise at –100ºC a solution of 1 (200 mg, 0.72 mmol) in 1 mL of THF. After stirring for 10 min at the above temperature, p-nitrobenzaldehyde (121 mg, 0.08 mmol) in 1 mL of THF was added dropwise. After 15 min, at –100ºC, the reaction mixture was quenched with aqueous (20%) AcOH, poured into water, and extracted with CH_2Cl_2. The extracts were washed successively with saturated NaHCO_3 solution and brine, dried (MgSO_4), and evaporated under reduced pressure. Chromatographic purification of the residue (ether/petroleum ether, 1:2) gave compounds 3–7, as viscous oils. Yields are reported in Table 1.

**2-Bromomethyl-4-(p-nitrophenyl)-3-benzenesulfonyl-1-buten-4-ol (syn) (3).** 1H NMR δ 8.18–8.08 (m, 2H), 7.94–7.85 (m, 2H), 7.76–7.48 (m 5H), 5.53–5.40 (m, 3H), 4.60 (d, J = 2 Hz, 1H), 4.13 (dd, J = 9, 1 Hz, 1H), 3.46 (dd, J = 11, 1Hz, 1H), 3.21 (dd, J = 11, 1H). 13C NMR δ 147.9 (s), 145.9 (s), 137.1 (s), 135.1 (s), 134.5 (d), 129.6 (d), 129.1 (d), 128.9 (d), 124.3 (t), 123.3 (d), 73.3 (d), 72.3 (d), 36.1 (t). M.S. (CH_4/CI) m/e (%): 443, 445 (MH^+, 84, 100), 363 (MH^+–HBr, 11); HRMS: calcd. (C_17H_17NO_5SBr, MH^+) 427.9990, 426.0010, found 427.9410, 425.9447.

**2-Bromomethyl-4-(p-nitrophenyl)-3-benzenesulfonyl-1-buten-4-ol (anti) (4).** 1H NMR δ 8.20–8.11 (m, 2H), 7.95–7.84 (m, 2H), 7.75–7.67 (m, 1H), 7.63–7.43 (m, 4H), 6.11 (s, 1H), 5.83 (BS, 1H), 5.67 (s, 1H), 3.95 (dd, J = 2.5, 1Hz, 1H), 3.83 (d, J = 2 Hz, 1H), 3.49 (dd, J = 11, 1 Hz, 1H), 3.18 (dd, J = 11, 1Hz, 1H). 13C NMR δ 147.6 (s), 145.9 (s), 136.7 (s), 134.5 (d), 129.6 (d), 129.1 (d), 128.9 (d), 124.3 (t), 123.3 (d), 73.3 (d), 72.3 (d), 36.1 (t). M.S. (ammonia/CI) m/e (%): 443, 445 (NH_3 MH^+), 50, 58), 363 (NH_3+MH^+–HBr, 100), 316 (NH_3+MH^+–HBr–HNO_2, 13).
4-Methylene-trans-2-(p-nitrophenyl)-3-benzenesulfonyltetrahydrofuran (5). $^1$H NMR $\delta$ 8.23–8.14 (m, 2H), 7.98–7.90 (m, 2H), 7.77–7.69 (m, 1H), 7.66–7.56 (m, 2H), 7.51–7.43 (m, 2H), 5.72 (d, J = 4 Hz, 1H), 5.32 (dt, J = 13, 1 Hz), 4.35 (dq, J = 13, 2Hz, 1H) 4.09–4.02 (m, 1H). 13C NMR $\delta$ 149.1 (s), 147.6 (s), 139.4 (s), 136.5 (s), 134.4 (d), 129.7 (d), 129.2 (d), 126.5 (d), 123.8 (d), 114.3 (t), 80.0 (d), 72.3 (t). M.S. (iso-butane/CI) m/e (%): 346 (MH$^+$, 21), 203 (M$^+$-HSO$_2$Ph, 100).

2-(p-Nitrophenyl)-3-benzenesulfonyl-4-(1'-p-nitrophenyl-2'-ethyl-1'-ol)-2,5-dihydrofuran (7). $^1$H NMR $\delta$ 8.32–8.24 (m, 2H), 8.15–7.99 (m, 2H), 7.72–7.63 (m, 2H), 7.50–7.48 (m, 2H), 7.44–7.37 (m, 2H), 7.30–6.63 (m, 4H), 5.91 (dd, J = 5.7, 3.7 Hz, 1H), 5.22 (dt, J = 7.4, 5.5 Hz, 1H), 5.00 (dd, J = 15.5, 5.5 Hz, 1H), 4.89 (dd, J = 15.5, 3 Hz, 1H), 3.24–3.14 (m, 3H). 13C NMR $\delta$ 152.0 (s), 150.5 (s), 148.1 (s), 147.7 (s), 145.6 (s), 139.6 (s), 136.5 (s), 133.9 (d), 129.1 (d), 128.8 (d), 127.2 (d), 126.3 (d), 124.0 (d), 123.4 (d), 87.6 (d), 79.2 (t), 72.1 (d), 35.6 (t). M.S. (ammonia/CI) m/e (%): 514 (MNH$_4^+$, 100), 449 (M$^+$-HNO$_2$, 52), 419 (MH$^+$-Ph, 46), 373 (MNH$_4^+$-SO$_2$Ph, 5).

General procedure for the reaction of aldehydes (2a–d) with 1-benzenesulfonyl-2-methylene-3-bromopropane (1); preparation of compounds (6a–d)

To a stirred solution of LDA (prepared from 0.07 mL (0.5 mmol) of diisopropylamine and 0.32 mL of n-BuLi (0.46 mmol, 1.475 N in hexane) in 2 mL of THF) was added dropwise at –100ºC a solution of 1 (100 mg, 0.36 mmol) in 0.5 mL of THF. After stirring for 10 min at the above temperature, the aldehyde 2 (a–d) (0.4 mmol) in 0.5 mL of THF was added dropwise. After addition of the aldehyde, a mixture of HMPA (0.5 mL) and THF (0.4 mL) was added dropwise at –100ºC. The mixture was stirred for an additional 3 h at –40ºC and then quenched with aqueous AcOH (20%), poured into water, and extracted with CH$_2$Cl$_2$. The extracts were washed successively with saturated NaHCO$_3$ solution and brine, dried (MgSO$_4$), and evaporated under reduced pressure. Chromatographic purification of the residue (petroleum ether/ether, 2:1) gave the desired product (6a–d).

4-Methyl-3-benzenesulfonyl-2-propyl-2,5-dihydrofuran (6a) was obtained from 1 and butyraldehyde (2a) as a viscous liquid (60 mg, 0.23 mmol, 63%). $^1$H NMR $\delta$ 7.94–7.83 (m, 2H), 7.70–7.51 (m, 3H), 4.99–4.85 (m, 1H), 4.67 (dd, J = 14, 5 Hz, 1H), 4.54 (dd, J = 14, 3 Hz, 1H), 2.15 (s, 3H) 1.86–1.46 (m, 2H), 1.39–1.12 (m, 2H) 0.85 (t, J = 7 Hz, 3H). 13C NMR $\delta$ 150.7 (s), 141.3 (s), 133.9 (s), 133.5 (d), 129.2 (d), 127.2 (d), 86.7 (d), 78.9 (t), 36.9 (t), 17.8 (t), 13.8 (q), 11.3 (q). M.S. (El) m/e (%): 267 (MH$^+$, 100), 223 (M$^+$-C$_3$H$_8$, 99) 141 (SO$_2$Ph$^+$, 37), 125 (SO$_2$Ph$^+$–O, 57), 77 (Ph$^+$, 78); HRMS calcd. (C$_{14}$H$_{19}$O$_3$S, MH$^+$) 267.1054, found 267.0881.

4-Methyl-3-benzenesulfonyl-2-pentyl-2,5-dihydrofuran (6b) was obtained from 1 and hexanal (2b) as a viscous liquid (55 mg, 0.19 mg, 52%). $^1$H NMR $\delta$ 7.94–7.83 (m, 2H), 7.69–7.50 (m, 3H) 5.00–4.87 (m, 1H), 4.67 (dd, J = 16, 5 Hz, 1H), 4.55 (dd, J = 16, 4 Hz, 1H), 2.15 (s, 3H) 1.92–1.04 (m, 8H), 0.84 (t, J = 6 Hz, 3H). 13C NMR $\delta$ 150.7 (s), 141.3 (s), 133.7 (s), 133.4 (d), 129.2 (d), 127.1 (d), 86.8 (d), 78.8 (t), 34.7 (t), 31.5 (t), 24.1 (t), 22.5 (t), 13.9 (q), 11.2 (q). M.S.
(EI) m/e (%): 295 (MH⁺, 97), 223 (MH⁻-C₅H₁₂, 100) 141 (SO₂Ph⁺, 28) 125 (SO₂Ph⁺–O, 23), 77 (Ph⁺, 76); HRMS calcd. (C₁₆H₂₅O₃S, MH⁺) 295.1367, found 295.1274.

4-Methyl-3-benzenesulfonyl-2-(p-tolyl)-2,5-dihydrofuran (6c) was obtained from 1 and p-tolyl-benzaldehyde (2c) as a white solid (96.4 mg, 0.306 mmol, 85%, m.p. 123.7°C). 1H NMR δ 7.51–7.39 (m, 1H), 7.32–7.17 (m, 4H), 6.99–6.89 (m, 4H), 5.93–5.87 (m, 1H), 4.88 (dd, J = 15, 5.5 Hz, 1H), 4.78 (dd, J = 15, 3.5 Hz, 1H), 2.29 (s, 6H). 13C NMR δ 150.5 (s), 141.0 (s), 138.4 (s), 136.0 (s), 135.7 (d), 128.9 (d), 128.6 (d), 127.9 (d), 127.3 (d), 89.0 (d), 79.7 (t), 21.2 (q), 11.4 (q). M.S. (iso-butane/CI) m/e (%): 332 (MH₂O⁺, 6) 315 (MH⁺, 13) 297 (MH⁺–H₂O), 8), 223 (M⁺–C₇H₇⁺, 100), 173 (M⁺–SO₂Ph⁺, 2).

4-Methyl-3-benzenesulfonyl-2-(p-nitrophenyl)-2,5-dihydrofuran (6d) was obtained from 1 and p-nitrobenzaldehyde (2d) as a yellow solid (60 mg, 0.173 mmol, 48%, m.p. 224.2°C). 1H NMR δ 8.02–7.94 (m, 2H), 7.51–7.19 (m, 7H), 6.05–5.97 (m, 1H), 4.96 (dd, J = 15, 5 Hz, 1H), 4.85 (dd, J = 15, 4 Hz, 1H), 2.33 (s, 3H). 13C NMR δ 151.8 (s), 148.0 (s), 146.0 (s), 134.4 (s), 133.3 (d), 128.8 (d), 127.0 (d), 123.3 (d), 87.9 (d), 80.1 (t), 11.4 (q). M.S. (iso-butane/CI) m/e (%): 346 (MH⁺, 100), 323 (MH⁺–H₂O), 58), 223 (M⁺–NO₂Ph⁺, 47), 204 (M⁺–SO₂Ph⁺, 62), 158 (M⁺–SO₂Ph⁺–NO₂Ph⁺, 9); HRMS calcd (C₁₇H₁₆NO₅S, MH⁺) 346.0749, found 346.0738.

General procedure for the reaction of hexanal (2b) with 1-benzenesulfonyl-2-methylene-3-hydroxypropane (8); preparation of compounds (10–11)

To a stirred solution of LDA (prepared from 0.17 mL (1.2 mmol) of diisopropylamine and 0.94 mL of n-BuLi (1.2 mmol, 1.475N in hexane) in 4 mL of THF) was added dropwise at –100°C a solution of 8 (100 mg, 0.48 mmol) in 1 mL of THF. After stirring for 10 min at the above temperature, the hexanal 2b (58 mg, 0.58 mmol) in 0.5 mL of THF was added dropwise. The mixture was stirred for an additional 1 h at –100°C and then quenched and extracted as described for 6(a–d). Chromatographic purification of the residue (petroleum ether / ethyl acetate, 1:1) gave products 10 and 11 (66 mg, 0.21 mmol, 44%) (10:11 = 1.28:1) as a viscous oil (inseparable mixture).

2-Methylene-3-(benzenesulfonyl)nonane-1,4-diol (10, syn) a and (11, anti) b. 1H NMR δ 7.91–7.83 (m, 2Ha, 2Hb), 7.72–7.48 (m, 3Ha, 3Hb), 5.47 (s, 1Hb), 5.40 (s, 1Ha), 5.36 (s, 1Hb), 5.03 (s, 1Ha), 4.93–4.46 (m, 3Ha, 3Hb), 3.85 (d, J = 9 Hz, 1Hb), 3.75 (d, J = 2 Hz, 1Ha), 3.68–3.59 (m, 1Ha, 1Hb), 2.91 (t, J = 6 Hz, 1Hb), 2.35 (t, J = 6 Hz, 1Ha), 1.66–1.13 (m, 8Ha, 8Hb), 0.94–0.79 (m, 3Ha, 3Hb), 13C NMR δ 139.5 (s, a), 137.7 (s, b), 137.5 (s, b), 137.1 (s, a), 134.0 (d, b), 133.9 (d, a), 129.1 (d, b), 129.0 (d, a), 128.9 (d, a), 128.7 (d, b), 123.9 (t, b), 119.5 (t, a), 73.2 (d, a), 72.4 (d, b), 70.3 (d, a), 68.5 (d, b), 65.6 (t, a), 65.3 (t, b), 34.5 (t, b), 34.3 (t, a), 31.5 (t, a), 31.4 (t, b), 25.3 (t, b), 24.7 (t, a), 22.5 (t, a), 22.4 (t, b), 13.9 (q, a, b). M.S. (CH₄/CI) m/e (%): 313 (MH⁺, 32), 295 (MH⁺–H₂O, 100), 277 (MH⁺–2H₂O, 8), 195 (M⁺–H₂O C₆H₁₂O, 10); HRMS: calcd. (C₁₆H₂₅O₄S, MH⁺) 313.1473, found 313.1378.
Acknowledgments

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References and Notes

6. The *syn-* and *anti-* nomenclature, used here, is the one proposed by Oare, D.A., Heathcock, C.H. *Topics in Stereochemistry*; Eliel, E.L., Wilen, S.H., Eds; Wiley: New York, 1990, Vol. 19, pp 227, for Michael additions. In such Michael adducts the extended chain contains the two anion-stabilizing groups. In the case of 3 and 4 the PhSO2 and the OH are part of the extended chain and the R- and allyl bromide substituents can be *syn-* or *anti-* oriented.
7. We are ignoring conformations in which the *p-*nitrophenyl group (R) is *gauche* to the two large groups (PhSO2 and allyl bromide).