O-Sulfinylation of Alcohols with Methanesulfonyl Cyanide or p-Toluenesulfonyl Cyanide.

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Abstract: Reaction of p-toluenesulfonyl cyanide or methanesulfonyl cyanide with alcohols in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,4-diazabicyclo[2.2.2]octane (DABCO) gives sulfinates in good yield. A mechanistic scheme involving sulfinyl cyanates 9 and 21 is suggested.

Introduction

Transformation of alcohols to the corresponding imidates in a base-catalyzed reaction with various nitriles is an important reaction in synthetic organic chemistry. This reaction has been known for almost a hundred years (Nef, 1895) and it has found application for several synthetic purposes. One major application is the use of imidates in glycoside and oligosaccharide synthesis. We have employed this method for the transformation of alcohols via their imidates to radicophilic thio- and selenocarbonyl derivatives for radical deoxygenation reactions. In an attempt to obtain tosyl imidates of various alcohols from the base-catalyzed reaction with the corresponding alcohol 2 and tosyl cyanide 1a we have found that the corresponding sulfinates 4 were formed instead of the desired imidates (3). This prompted us to study this new reaction in detail and attempt to prove the mechanism.
We have extended this new reaction by using methanesulfonfonyl cyanide 1b instead of p-toluenesulfonfonyl cyanide. We found that 1b gave methanesulfinates 5 in high yield. The yields of this reaction were comparable to or higher than those of the corresponding p-toluenesulfinates⁴⁻⁵.

O-Sulfinylation

Known methods for the synthesis of sulfinyl esters require the activation⁶⁻⁷ of sulfinic acids, or the use of the corresponding sulfinyl chlorides⁸⁻⁹. A recent report describes a one-pot synthesis of sulfinates from alcohols with sulfinyl chlorides and trimethyl phosphite¹⁰. The latter method, however, gives methanesulfinates in a lower yield⁴.

Radical deoxygenation of alcohols¹¹ (the Barton-McCombie reaction) can be carried out on derivatives of alcohols containing a thio- or selenocarbonyl moiety. In most systems this functionality is the most radicophilic, thereby directing the attack of the radical reagent to the derivatized alcohol. There are numerous reagents¹² for the transformation of alcohols to thiocarbonyl derivatives suitable for this radical process. As a continuation of our research in this field we reacted various alcohols with tosyl cyanide 1a (Scheme 1) in the presence of a base (DBU) to form the imidates 3. However, sulfinates 4 have been obtained in high yield, instead of 3. The sulphinates 4 formed in our reactions have been identified (in addition to physical methods) by comparison with authentic compounds and also by oxidizing them to the known sulfonates (tosylates).

A thorough study showed that primary, secondary and tertiary alcohols furnish p-toluenesulfinates upon treatment with DBU or DABCO and 1a. Methanesulfonfonyl cyanide 1b gave the corresponding methanesulfinates 5 in high yields (all the yields are given in the Experimental section).

![Scheme 1](image_url)
Tosyl cyanide is easily cleaved in homolytic\textsuperscript{5,19,20,21} or heterolytic processes\textsuperscript{13}. With nucleophiles (ArO\textsuperscript{-}, RS\textsuperscript{-}, R\textsubscript{2}N\textsuperscript{-}, ArMgX) it gives ArOCN, RSCN, R\textsubscript{2}NCN, ArCN-type products. The only other product of our reactions is TsS-4Me-Ph\textsuperscript{14} \textsuperscript{13}. This suggests a more complicated mechanism.

A possible mechanistic pathway leading to this new reaction is depicted in Scheme 2 and 3.
Thus treatment of a sulfonyl cyanide (1a) with a strong, non-nucleophilic base (in this case DBU or DABCO) would give via intermediates 7 and 8 the cyanate 9. We assumed that this cyanate 9 was responsible for the sulfinyl transfer to the given alcohols present resulting in the formation of the corresponding p-toluenesulfinates 4. Blank experiments of tosyl cyanide and DBU or (DABCO) resulted in the formation of 13 (25%) most probably in accordance with Scheme 3.

In the presence of an alcohol the activated sulfinyl moiety of 9 can be transformed to sulfinates (4), or the weak S-O single bond may undergo homolytic cleavage giving sulfinyl radicals 11. In the absence of alcohols or radical traps the formation of the thiosulfonate (13) can be interpreted as a self termination of 1115 (Scheme 3).

One may suggest that 13 could possibly take part in the formation of sulfinates 4 in accordance with the Scheme 4.

We have therefore studied the reaction of 13 and cyclododecanol (2a) in the presence of DBU. However, reaction of 2 equivalents of 13 with 1 equivalents each of DBU and 2a resulted in the formation of only 20% of cyclododecanol p-toluenesulfinate (4a) (24hr), and the known 4-tolyl-disulfide (15) (30%). This sulfinylation is much slower and gives much lower yields than the reaction of tosyl cyanide (1a) and alcohols in the presence of DBU (reaction time: 2hr). Moreover, we could not detect the disulfide (15) in the latter. These findings suggest that O,S-sulfinyl-sulfinates of type 14 are not intermediates in the sulfinylation reaction of 1a in the presence of DBU. In order to corroborate our suggested mechanistic scheme of the sulfinylation reaction of 1a (Scheme 3), we attempted to detect the other product HOCl (6). Therefore we attempted the known reaction16 of the cyanate anion with benzyl chloride and ethyl alcohol in DMF. Indeed, in the one-pot procedure (sulfinylation, followed by the addition of benzyl chloride and ethanol) we have obtained the benzyl urethane 10 (97% yield, g.l.c.).

\[
\begin{align*}
\text{Me} & - \text{SO} - \text{S} - \text{Me} \\
\text{Me} & - \text{SO} - \text{S} - \text{Me}
\end{align*}
\]

\[\rightarrow \]

\[
\begin{align*}
\text{Me} & - \text{SO} - \text{S} - \text{Me} \\
\text{Me} & - \text{SO} - \text{S} - \text{Me}
\end{align*}
\]

Scheme 4

In order to find further evidence of the radical cleavage of the suggested intermediate 9, we have attempted to use mixed anhydrides of \(\text{N}\)-hydroxy-2-thiopyridone (like 16), known thermal or photolytic sources of carbon radicals17. When used alone in darkness, neither DABCO nor 1a initiated the radical rearrangement of 16 to 17.
However, when 16 was treated in the dark with both DABCO and 1a, 19 was isolated in 17% yield; undoubtedly formed from the phenylethyl radical 18. In a similar reaction 1b gave 20.

NMR experiments

$^{13}$C NMR experiments

The progress of the rearrangement of tosyl cyanide 1a in the presence of an equimolar amount of DABCO was followed by $^{13}$C NMR at low temperature. DABCO was added into the tube containing the solution of 1a at -60°C and $^{13}$C NMR spectra were recorded at -60, -50, -40, -30, -20, -10, 0 and 20°C. We have found that the reaction between tosyl cyanide 1a and the base takes place at temperatures higher than -50°C. At -40°C the peaks of 1a completely disappear and a new set of peaks appear corresponding to the cyanate 9. The most characteristic change is, as expected, the disappearance of the CN carbon at 113.6 ppm and the appearance of a new carbon at 152.5 ppm that is attributed to the OCN carbon of 9. This intermediate 9 is stable in the absence of alcohols up to -20°C. At that temperature it disappears, due to the homolytic cleavage of 9.

The same experiment was repeated with methanesulfonyl cyanide 1b. In this case the rearrangement takes place upon the addition of DABCO at -60°C. The carbon peaks of 1b (45.6 and 112.6 ppm) change to those of the corresponding cyanate (42.4 and 156.6 ppm). This change is similar to that, observed in the case of 1a. We have found that this intermediate sulfinyl cyanate 21 is stable up to -50°C. At -40°C this intermediate can no longer be detected. The cyanate peak (152.5 ppm) disappears at -40°C. The methyl signal of the intermediate methanesulfinyl cyanate 21 also disappears at -40°C, being replaced by that of the corresponding thiosulfonate 22.
Low temperature $^{13}$C NMR experiment in the presence of an alcohol.

DABCO (1.1 eq.) was added carefully to methanesulfonfyl cyanide 1b (1.0 eq.) in an NMR tube at -60°C. The $^{13}$C NMR spectrum showed the complete disappearance of 1b and the appearance of the peaks of 21 as seen previously. Cyclohexadecanol (0.8 eq.) was then added at -60°C. The $^{13}$C NMR spectrum of the crude mixture showed clearly the peaks of the corresponding methanesulfinate 5a. The peaks of the intermediate methanesulfinyl cyanate 21 disappeared indicating that 5a was indeed formed from 21.

Independent preparation of $p$-toluenesulfinyl cyanate 9 and methanesulfinyl cyanate 21.

$p$-Toluenesulfinic acid$^6$ was dissolved in CDCl$_3$ and the $^{13}$C spectrum was recorded at -60°C. This solution was then treated with DABCO, followed by cyanogen bromide. The $^{13}$C NMR spectra of this reaction mixture were then recorded at -60, -50, -40, -30, -20, -10, 0 and 20°C respectively. The $^{13}$C peaks of 9 (immediately appeared at -60°C and disappeared at -20°C) are in good agreement with those, seen in the $p$-toluenesulfonyl cyanide + DABCO reaction (Scheme 5).

![Scheme 5](image)

A) 9 formed in the TsCN + DABCO reaction mixture.  
B) 9 formed in the 4-MePhSO$_2$H + DABCO + BrCN reaction mixture.

![Scheme 6](image)

A) 21 formed in the MsCN + DABCO reaction at -60°C.  
B) 21 formed in the MeSO$_2$H + DABCO + BrCN reaction at -60°C.
Similarly, treatment of methanesulfinic\(^{18}\) acid with DABCO and cyanogen bromide at -60°C we have observed the appearance of a peak in the \(^{13}\)C NMR spectrum at 155.7 ppm. This can be attributed to the formation of the sulfinyl cyanate. The corresponding value observed in the rearrangement of methanesulfanyl cyanide was 156.6 ppm. In both cases these peaks disappear above -40°C, indicating that these compounds are thermally unstable but can be made and used at -60°C (Scheme 6).

**Experimental**

\(^1\)H and \(^{13}\)C NMR spectra were recorded on a Varian XL-200E spectrometer for deuterochloroform solutions (δ scale, TMS as internal standard). Variable temperature \(^{13}\)C NMR measurements were carried out on a Varian XL-200 spectrometer. Mass spectra (70 eV; electron impact) were obtained using a Hewlett-Packard 5995C quadrupole GC-MS instrument. IR spectra were measured with a Perkin-Elmer 881 spectrometer; only the most significant absorptions are listed. GIC analyses were performed with a Chrompack 439 instrument equipped with a FID detector and a DB-5 (0.1 mm) fused silica capillary column (30m x 0.25 mm) using nitrogen as carrier gas, and naphthalene as internal standard. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA. Melting points were determined on a Kofler hot stage and are uncorrected. N-Hydroxy-pyridine-2-thione was prepared from the 40% aqueous solution of its sodium salt (trade name: sodium Omadine\(^{8}\) a kind gift from the Olin Corporation).

**Structures of the starting alcohols** 2a-g

\[ \text{Structures of the starting alcohols} \]

\[ \text{2a-g} \]

**General procedure for the synthesis of sulfinates 4 from the tosyl cyanide 1a:**

To the solution of the starting alcohol 2 (2 mmol) in dry dimethylene dichloride (5-8 ml), DBU was added under argon at 0-5°C (ice bath), followed by the addition of tosyl cyanide (1a) in small portions. Then the pale yellow solution was allowed to warm up to room temperature and the reaction monitored by t.l.c. The reaction was complete in less than 2 hr. Then the mixture was concentrated in vacuum and the title compounds isolated by column chromatography on silica gel (hexanes: ether 8:2).

Compound 4a: Yield: 89% (from dimethylene dichloride:hexanes), mp. 51-52°C; IR (CHCl\(_3\)) 1126 cm\(^{-1}\) (S=O); \(^1\)H NMR (δ): 1.1-1.9 (22 H, m, CH\(_2\) groups), 2.4 (3 H, s, Me), 4.5 (1 H, m, H-1), 7.33 (2 H, d, J =
8Hz), 7.63 (2 H, d, J = 8Hz); 13C NMR (δ): 20.0, 21.6, 23.5, 24.0, 24.2, 24.4, 30.9, 31.0, 78.2, 125.1, 129.7, 142.6, 143.2. m/z (%): 322 (0.3), 306 (1.6), 157 (100); HR-MS m/z = 322.1962, [calc. for C25H44O2S: 322.1966]. Compound 4a was identical with the product obtained by the reported procedure.10

Compound 4b: Yield: 85% (from methylene dichloride: hexanes), mp. 130-131°C (lit.6 123-135°C, chloroform: methanol); 1H NMR (δ): 2.41 (6 H, s), 4.1-4.25 (2 H, m), 5.3 and 5.41 (2 H, m), 7.32 (4 H, d, J = 8Hz), 7.62 (4 H, d, J = 8Hz).

Compound 4c: Yield: 91% (from methylene dichloride: hexanes), mp. 118-120°C (lit.6 121-123°C, chloroform: methanol); 1H (δ): 2.42 (3 H, s), 4.2-4.35 (1 H, m), 7.32 (2 H, d, J = 8Hz), 7.61 (2 H, d, J = 8Hz).

Compound 4d: Yield: 94%; mp. (of the (S)-(–) menthyl p-toluensulfinate) 102-104°C (lit.6 103-105°C); 1H (δ): 2.42 (3 H, s), 3.95-4.4 (1 H, dt, Jaa = 10.5Hz, Jae = 4Hz), 7.34 (2 H, d, J = 8Hz), 7.68 (2 H, d, J = 8Hz).

Compound 4e: Yield: 92% (from ether: hexanes), mp. 37-38°C; IR (CHCl3) 1130 cm⁻¹ (S=O); 1H (δ): 0.8-1.8 (35 H, m), 2.41 (3 H, s, Me), 3.5-3.7 and 3.9-4.1 (2 H, dt, J1 = 7Hz, J2 = 10Hz), 7.32 (2 H, d, J = 8Hz), 7.61 (2 H, d, J = 8Hz); 13C (δ): 14.2, 21.6, 22.8, 25.8, 29.3, 29.5, 29.6, 29.7, 29.8, 32.1, 64.6, 125.3, 129.8, 142.0, 142.6; m/z (%): 408 (0.3), 253 (3), 157 (100); HR-MS m/z=408.3065, [calc. for C25H44O2S: 408.3062].

Compound 4f: Yield: 91%; IR (CHCl3): 1130, 1140 cm⁻¹ (S=O); 1H (δ) (major): 1.2-1.6 (4 x 3 H, 4s), 2.44 (3 H, s), 3.9-4.3 (3 H, m), 4.76 (1 H, d, J = 3.6Hz), 4.95 (1 H, d, J = 3Hz), 5.85 (1 H, d, J = 3.6Hz), 7.37 (2 H, d, J = 8Hz), 7.68 (2 H, d, J = 8Hz), (minor): 1.2-1.6 (4 x 3 H, 4s), 2.44 (3 H, s), 3.9-4.3 (3 H, m), 4.51 (1 H, d, J = 2.4Hz), 4.82 (1 H, d, J = 3.5Hz), 5.92 (1 H, d, J = 3.3Hz), 7.35 (2 H, d, J = 8Hz), 7.65 (2H, d, J = Hz); m/z(%): 399 (0.1), 383 (22), 139 (100).

Compound 4g: Yield: 87.5% (from methylene dichloride: hexanes), mp. 81-82°C (lit.6 80-82°C); 1H: 1.7-2.3 (15 H, m), 2.45 (3 H, s), 7.30 (2 H, d, J = 8Hz), 7.60 (2 H, d, J = 8Hz).

p-Tolyl p-toluensufonosulfinate14: 13: Yield:36%; mp. 74-76°C (lit.14 74-76°C); 1H (δ): 2.35 (3 H, s), 2.45 (3 H, s), 7.15 (2 H, d, J = 8Hz), 7.20 (2 H, d, J = 7Hz), 7.25 (2 H, d, J = 7Hz), 7.45 (2 H, d, J = 8Hz).

An authentic specimen was prepared according to the literature procedure.14

Oxidation of p-toluensufonates to p-toluencesulfonates: Typical procedure: To a solution of the appropriate p-toluensulfonate 4 (0.5 mmol) in dry chloroform (5 ml) 60% mCPBA (0.210g, 1.0mmol) was added at 0°C in small portions. The reaction was monitored by t.l.c. When all the sulfonate was consumed, the reaction mixture was extracted with sat. aqueous sodium bicarbonate and dichloromethane and the organic layer dried over anhydrous magnesium sulfate. Removal of most of the solvents and dropwise addition of hexanes afforded the known tosylates in high yield.
**Independent preparation of the p-toluenesulfonates:** Typical procedure: The alcohol 2 (2.5 mmol) was dissolved in dry pyridine (20 ml) at 0°C and treated with tosyl chloride (1.42 g, 7.5 mmol) added in small portions. After stirring overnight, the solvent was evaporated under vacuum and the residue was extracted with dichloromethane and water. The organic layer was dried over magnesium sulfate and concentrated under vacuum. Gradual addition of hexanes afforded the known tosylates in high yield.

**Cyclohexyl p-toluenesulphonate**

Yield: 89%; mp. 88-89°C; 
$^1$H (δ): 1.1-1.8 (23 H, m), 2.4 (3 H, s), 4.65 (1 H, m), 7.31 (2 H, d, J = 8Hz), 7.80 (2 H, d, J = 8Hz).

**3β-cholestanyl p-toluenesulphonate**

Yield: 85%; mp. 135-136°C; 
$^1$H (δ): 0.5-2.0 (m, cholest.), 2.4 (3 H, s), 4.45 (1 H, m), 7.30 (2 H, d, J = 8Hz), 7.80 (2 H, d, J = 8Hz).

**Reaction of the cyclohexyl alcohol 2a with 13 in the presence of DBU:** To a solution of the alcohol 2a (0.5 g, 2.7 mmol) in 20 ml dry dichloromethane were added DBU (0.42 g, 2.7 mmol) followed by compound 13 (1.5 g, 5.4 mmol) in small portions. Stirring was continued at room temperature for 24 hr and the reaction was followed by t.l.c. The solvent was then concentrated and the mixture separated on silica gel using hexanes:ether (in gradient) as eluent. The p-tolyl disulfide 15 has been isolated in 30% yield together with compounds 4a (20%), 13 (52%) and 2a (73%).

**p-Tolyl disulfide 15**; mp. 42-44°C. The spectral data of this compound were identical to those reported for the commercial product (Aldrich, 98%).

**Synthesis of the benzylurethane 10:** The title compound was synthesized according to the literature procedure in 65% yield, mp. 42-43°C (lit. 41.5-42°C).

**Synthesis of the benzylurethane 10 in situ:** The alcohol 2a (0.1 g, 0.54 mmol) was dissolved in 4 ml dry dichloromethane at 0°C and treated with DBU (90 mg, 0.59 mmol) followed by tosyl cyanide 1a (0.38 g, 2.1 mmol) in small portions. The disappearance of the alcohol was followed by t.l.c. After the end of the reaction 37.3 mg (0.81 mmol) of absolute ethanol and 82 mg (0.64 mmol) of freshly distilled benzyl chloride were added and the reaction mixture was kept boiling for 3 hr. Glc analysis of the crude reaction mixture (an authentic sample was prepared and used for comparison) indicated a 97% yield of the in situ prepared benzylurethane 10.

**Glc conditions:** 1μl samples were injected at once at an oven temperature of 80°C for one minute. After the temperature was increased to 250°C at a rate of 15°C/min. Retention times: 5.80 min (int. standard) and 8.75 min (urethane 10).

**Trapping experiments of the intermediate 9:**

Using the acyl N-hydroxy-2-thiopyridone 16: Tosyl cyanide 1 (100 mg, 0.55 mmol) and compound 16 (0.43 g, 1.6 mmol) were placed in a flask covered with aluminum foil, under argon in 15 ml dry dichloromethane,
followed by addition of DABCO (30 mg, 0.28 mmol) in one portion. The reaction mixture was stirred at 0°C for 3 hr; then the solvent was distilled under vacuum. The residue was purified on silica gel (hexanes: ether 80:20) to give the sulfide 19 in 17% yield as a pale yellow oil. The independent preparation of the sulfide 19 was carried out according to the literature procedure in 92% yield. The same reaction of 1b gave the sulfide 20 in 7% yield.

b: Using cyclohexene according to the known procedure: Tosyl cyanide 1a (100 mg, 0.55 mmol), (0.82 g, 10 mmol) of freshly distilled cyclohexene and 2 ml of dry dichloromethane were placed in a flask under argon. The flask was covered with aluminum foil to protect the reaction mixture from light. DABCO (30 mg, 0.27 mmol) was then added and the reaction mixture was stirred at room temperature for 3 hr. The solvent was removed in vacuum. 1H NMR analysis of the crude mixture showed no evidence of adducts containing the cyclohexyl moiety.

Preparation of the mixed anhydride of N-hydroxy-2-thiopyridone 16 was carried out according to the literature procedures.

**General procedure for the synthesis of methanesulfinates 5 from 1b and 2:**

To the solution of the starting alcohol 2 (2 mmol) in dry methylene dichloride (8-10 ml) DBU (1.1 eq., 2.2 mmol, 0.33 g, 0.33 ml) was added under argon at 0°C followed by dropwise addition of methanesulfonyl cyanide (1.5 eq., 3 mmol, 0.32 g). The pale yellow solution was allowed to warm up to room temperature and monitored by TLC. When the reaction was finished (TLC) the mixture was concentrated in vacuum and the products isolated by column chromatography on silica gel (hexanes: ether = 8 : 2).

**Compound 5a:** Yield: 92% (from hexanes), mp. 26-27°C; IR (CHCl₃) 1114 cm⁻¹ (S=O); ¹H NMR (δ): 1.3-1.9 (22 H, m, CH₂ groups), 2.60 (3 H, s, Me), 4.3-4.4 (1 H, m, H-1); ¹³C NMR (δ): 20.7, 20.8, 23.1, 23.2, 23.3, 24.0, 24.3, 30.4, 30.8, 44.7, 79.1; m/z (%): 167 (8), 55 (100); calcd. for C₁₃H₂₆O₂S: C: 63.37, H: 10.63, found: C: 63.46, H: 10.67%.

**Compound 5b:** Yield: 91% (from hexanes/ether); mp.: 111-115°C (lit. mp.: 97-112°C); IR (CHCl₃) 1110 cm⁻¹(S=O); ¹H NMR (δ): 0.65-2.51 (43 H, m), 2.62 (3 H, s, Me), 4.0-4.2 (1 H, m), 5.39 (1H, m); ¹³C NMR (δ): 44.8 (Me), 80.0 (C-3); m/z (%): 386 (25), 368 (100).

**Compound 5c:** Yield: 98% (from ether/pentane), mp. 83-85°C, IR (CHCl₃) 1119 cm⁻¹(S=O); ¹H NMR (δ): 0.6-2.1 (46 H, m), 2.60 (3 H, s, Me), 4.1-4.2 (1 H, m); ¹³C NMR (δ): 44.7 and 44.9 (Me), 79.7, 79.9 (C-3); m/z (%): 264 (25), 55 (100); calcd. for C₂₈H₅₀O₂S: C: 74.61, H: 11.18, found: C: 74.45, H: 11.14%.

**Compound 5d:** Yield: 93%; IR (CHCl₃) 1123 cm⁻¹(S=O); ¹H NMR (δ): 0.75-2.24 (18 H, m), 2.60 (3 H, s, Me), 2.62 (3H, s), 3.71-4.01 (2 H, m).

**Compound 5e:** Yield: 91% (from ether/hexanes), mp. 38-39°C, IR (CHCl₃) 1123 cm⁻¹(S=O); ¹H NMR (δ): 0.85-0.95 (t, 3H, J = 7 Hz), 1.2-1.75 (32 H, m), 2.62 (3H, s), 3.95-4.05 (2 H, m); ¹³C NMR (δ): 14.2,
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22.8, 25.8, 29.3, 29.7, 29.8, 30.2, 32.0, 44.2, 68.5; m/z (%): 315 (10), 99 (30), 57 (100); calcd. for C_{19}H_{46}O_{2}S: C: 68.62, H: 12.12, found: C: 68.69, H: 12.06%.

Compound 5f: Yield: 84%, mp. 79-82°C (from ether/pentane); IR (CHCl₃) 1074, 1135 cm⁻¹ (S=O);¹H NMR (δ): 0.85-0.95 (t, 3H, J = 7 Hz), 1.31, 1.34, 1.43, 1.51 (4 x 3H, s), 2.689, 2.693 (2 x 3H, s), 4.0-4.3 (4 H, m), 4.6 (1H, d, J = 3.5 Hz), 4.8 (d1H, d, J = 2.0 Hz), 5.9 (1H, d, J = 3.5 Hz);¹³C NMR (δ): 25.2, 25.3, 26.2, 26.3, 26.6, 26.7, 26.8, 26.9, 44.3, 44.8, 66.8, 67.6, 72.2, 72.3, 76.5, 77.2, 77.8, 78.2, 80.3, 80.7, 83.0, 83.8, 83.9, 105.0, 105.3, 109.3, 109.4, 112.4; m/z (%): 307 (50), 249 (20), 127 (25), 101 (100); calcd. for C_{13}H_{22}O_{2}S: C: 48.44, H: 6.88, found: C: 48.55, H: 6.90%.

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References


