Palladium-Catalyzed Intramolecular Metallo-Ene Reactions Using Allylic Sulfoxides as Enophiles

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Palladium-catalyzed intramolecular metallo-ene reactions were studied using allylic sulfoxides as enophiles. Palladium-catalyzed reactions of allylic acetates and methyl carbonates bearing allylic sulfoxides at appropriate sites were carried out in acetic acid at 80°C to give cyclized products, cyclohexane derivatives, with extremely high diastereoselectivity. The stereochemistry of these reactions was examined under various reaction conditions using several model compounds.

Keywords: palladium catalyst; metallo-ene reaction; allylic acetate; allylic sulfoxide; sulfinate-sulfone rearrangement; stereoselectivity

Ene reactions have received much attention owing to their high diastereo- and enantioselectivity in carbon–
carbon bond formations. In particular, intramolecular ene reaction should be a useful tool for stereoselective
construction of cyclic compounds.

Transition metal-promoted carbon–carbon bond for-
mation reactions also offer high stereoselectivity and
toform new carbon–carbon bonds. However, π-allylpalladium complexes sometimes undergo metallo-ene reactions with olefins as enophiles. We report here diastereoselective
cyclizations by means of intramolecular metallo-ene re-
actions using allylic sulfoxides as enophiles.

Synthesis of Model Compounds: Model compounds for
intramolecular metallo-ene reactions were prepared as
follows. Dimethyl (4-acetoxy-2(Z)-butenyl)propanedioate (1a)
was obtained in 72% yield by the action of dimethyl
malonate sodium enolate with 4-acetoxy-2(Z)-butenyl
bromides which was prepared in situ by bromination of
4-acetoxy-2(Z)-butenol with N-bromosuccinimide (NBS)–
triphenylphosphine (PPh₃). Alkylation of 1a with 4-
(tetrahydro-2H-pyran-2-yl)dioxo-2(Z)-butenyl bromide was
carried out in tetrahydrofuran (THF) at 0°C for 1 h in
the presence of sodium hydride to give dimethyl (4-
acetoxy-2(Z)-butenyl)[4-(tetrahydro-2H-pyran-2-yl)dioxo-
2(Z)-butenyl]propanedioate (2a) in 72% yield. Treatment of
2a with pyridinium p-toluenesulfonate (PPTS) in
methanol at room temperature for 12 h gave dimethyl
(4-acetoxy-2(Z)-butenyl)[4-hydroxy-2(Z)-butenyl]propaned-
edioate (3a) in 85% yield. Sulfinylation of 3a with p-
toluenesulfinyl chloride was carried out in THF at 0°C
for 0.5 h in the presence of triethylamine to give dimethyl
(4-acetoxy-2(Z)-butenyl)[4-p-toluenesulfonfyl-oxy-2(Z)-
butenyl]propanedioate (4a) in 85% yield.

The reaction of 1a with 4-(tetrahydro-2H-pyran-2-
yl)dioxo-2(E)-butenyl bromide followed by treatment of the
malonate derivative 6a produced with PPTS and the
sulfinylation of the resulting alcohol 7a with p-toluene-
sulfonil chloride gave a sulfinate, 8a.

The methoxyoxoloxyl group of compound 1b was obtained
by the reaction of dimethyl malonate sodium enolate with
4-methoxyoxoloxyl-2(Z)-butenyl bromide. The reaction of
1b with 4-(tetrahydro-2H-pyran-2-yl)dioxo-2(Z) or
E)-butenyl bromide was carried out in THF at 0°C for
1 h using sodium hydride as a base to give 2b or 6b in 80
or 70% yield, respectively. The same reaction sequences
of 2b and 6b as described above gave 4b and 8b.

Chart 1

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Upon heating at 115 or 125°C in N,N-dimethylformamide (DMF), the sulfinates 4a and 8a, or 4b and 8b underwent sulfinate-sulfone rearrangements to afford dimethyl (4-acetoxy- or methoxycarbonyloxy-2(Z)-butenyl)(2-p-toluenesulfonyl-3-butenyl)propanedioate (5a, b) in 79—91% yields. A much higher reaction temperature (125°C) was required for the rearrangement of the (Z)-allylic sulfinates 4a, b.

The model compound, dimethyl (4-acetoxy-3-methyl-2(E)-butenyl)(2-p-toluenesulfonyl-3-butenyl)propanedioate (18), was prepared as follows. Regioselective allylic oxidation\(^\text{a, b}\) of 1-(tetrahydro-2H-pyran-2-yl)oxy-3-methyl-2-butenol (9) with selenium dioxide and tert-butyl perhydroxide (in dichloromethane, at room temperature, for 12 h, 45% yield) followed by acetylation of the resulting alcohol 10 with acetic anhydride afforded 4-(tetrahydro-2H-pyran-2-yl)-2-ethylpentyl acetate (11). Deprotection of the tetrahydropyran group with PPTS followed by bromination of the alcohol 12 with NBS-PPh\(_3\) gave 4-acetoxy-3-methyl-2(E)-butenyl bromide (13). Alkylation of dimethyl malonate sodium enolate with the bromide 13 (in THF, at 0°C, for 1 h) produced dimethyl (4-acetoxy-3-methyl-2(E)-butenyl)propanedioate (14) in 89% yield. The reaction of 14 with 4-(tetrahydro-2H-pyran-2-yl)oxy-2(Z or E)-butenyl bromide was carried out in THF at 0°C for 1 h using sodium hydride as a base to give dimethyl (4-acetoxy-3-methyl-2(E)-butenyl)[4-(tetrahydro-2H-pyran-2-yl)oxy-2(Z or E)-butenyl]propanedioate (15a, b) in 84 or 90% yield, respectively. The same reaction sequences of 15a, b as described earlier gave the sulfinates 17a, b. Heating of 17a, b at 115 and 125°C in DMF gave 18 in 93 and 90% yields, respectively.

**Intramolecular Metallo-Ene Reactions** The allylic sulfone 5a underwent an intramolecular metallo-ene reaction to give dimethyl cis- and trans-4-methylene-3-p-toluenesulfonyl-5-vinyl-1,1-cyclohexanedicarboxylate (19a, b), upon heating at 80°C in acetic acid for 4 h in the presence of a palladium catalyst, bis(dibenzylideneacetone)palladium [Pd(dbaza)] or tetrakis(triphenylphosphine)palladium [Pd(PPh\(_3\))] with or without a phosphine ligand (PPh\(_3\)). The results are summarized in Table I.

<table>
<thead>
<tr>
<th>8</th>
<th>Catalyst (mol%)</th>
<th>PPh(_3) (mol%)</th>
<th>Yield (%)*</th>
<th>Ratio of 19a to 19b</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>Pd(dbaza) (5)</td>
<td>15</td>
<td>24 (66)</td>
<td>83:17</td>
</tr>
<tr>
<td>8a</td>
<td>Pd(dbaza) (10)</td>
<td>30</td>
<td>26 (36)</td>
<td>63:37</td>
</tr>
<tr>
<td>8b</td>
<td>Pd(PPh(_3)) (10)</td>
<td>—</td>
<td>12 (47)</td>
<td>82:18</td>
</tr>
<tr>
<td>8b</td>
<td>Pd(dbaza) (5)</td>
<td>15</td>
<td>25 (32)</td>
<td>80:20</td>
</tr>
<tr>
<td>8b</td>
<td>Pd(dbaza) (10)</td>
<td>30</td>
<td>17 (67)</td>
<td>67:33</td>
</tr>
<tr>
<td>8b</td>
<td>Pd(PPh(_3)) (5)</td>
<td>—</td>
<td>22 (82)</td>
<td>83:17</td>
</tr>
<tr>
<td>8b</td>
<td>Pd(PPh(_3)) (10)</td>
<td>—</td>
<td>19 (22)</td>
<td>81:19</td>
</tr>
</tbody>
</table>

*The palladium-catalyzed reactions of 8a, b were carried out in AcOH at 80°C for 4 h. *b) The corrected yields based on the recovered starting material are given in parentheses.

The stereochemistry of the products 19a, b was determined on the basis of the NMR spectral data. A nuclear Overhauser effect (NOE) was observed between the hydrogen atoms at the C\(_3\) and C\(_5\) positions in the NMR spectrum of 19a, whereas such NOE was not observed in that of 19b. The ratio of the two products (19a, b) determined by high performance liquid chromatographic (HPLC) analysis, was dependent on the reaction conditions employed, the species of the catalyst and the molar amount of the catalyst and the ligand. The cis isomer 19a was preferentially (63—83%) formed under the reaction conditions examined. Similar results were ob-
tained with the acetoxy 5a and the methoxycarbonyloxy compound 5b.

In the palladium-catalyzed reaction of 18, high stereoselectivity was observed. The allylic sulfone 18 was treated with a catalytic amount of a palladium catalyst, Pd(dbaba)₂ or Pd(PPPh₃)₄, in acetic acid at 80 °C for 4 h to give dimethyl cis- and trans-5-isopropenyl-4-methylene-3-p-toluensulfonyl-1,1-cyclohexanedicarboxylate (20a, b) with extremely high diastereoselectivity (88–96% diastereomeric excess). The ratios of the products 20a, b were determined by HPLC analysis. The results obtained under various reaction conditions are summarized in Table II.

Similarly, the stereochemistry of the products 20a, b was determined by NMR spectral analysis; NOE was observed between the hydrogen atoms at the C₃ and C₅ positions in the NMR spectrum of 20a, but not in that of 20b. In contrast to the afore-mentioned cyclization of 5a, b, the methyl group of the isopropenyl substituent is highly effective for obtaining high diastereoselectivity.

**Stereochemistry of Palladium-Catalyzed Cyclizations of Allylic Sulfones** Palladium catalysts were reacted with allylic systems (5a, b and 18) at the reactive allylic sites (allylic acetates and methyl carbonate) to form π-allylpalladium complexes. In the six-membered transition states 22a–c for the metallo-ene cyclization, the transition state 22c with an axial p-toluensulfonyl group suffers extremely severe steric hindrance, particularly between the p-toluensulfonyl group and the ester. Therefore, the palladium complexes were reacted with intramolecular olefins and underwent metallo-ene cyclizations preferentially via the six-membered transition states 22a, b having equatorially orientated bulky groups (p-toluensulfonyl), giving 24a, b through reductive elimination of palladium in 23a, b. Since the conformation of 22a has rather severe steric hindrance due to the cis confusion, the metallo-ene reaction would occur preferentially via 22a to give 24a as a major product. In particular, extremely high diastereoselectivity was observed in the case of 21 (R = CH₃), owing to the steric effects of the sterically bulky isopropenyl group in 22b.

Thus, the products formed were controlled by the stereochemical environment in the transition states (22a, b) for cyclization without any equilibration between 24a and 24b in the presence of the palladium catalysts via π-allylpalladium complexes of the allylic sulfonyl parts.

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**Table II. Stereochemical Studies on Palladium-Catalyzed Cyclizations of Allylic Sulfone 18²**

<table>
<thead>
<tr>
<th>Catalyst (mol%)</th>
<th>PPh₃ (mol%)</th>
<th>Yield (%)³⁰</th>
<th>Ratio of 20a to 20b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(dbaba)₂ (5)</td>
<td>15</td>
<td>31 (75)</td>
<td>95:5</td>
</tr>
<tr>
<td>Pd(dbaba)₂ (10)</td>
<td>30</td>
<td>29 (84)</td>
<td>94:6</td>
</tr>
<tr>
<td>Pd(PPPh₃)₂ (5)</td>
<td>—</td>
<td>21 (59)</td>
<td>96:4</td>
</tr>
<tr>
<td>Pd(PPPh₃)₂ (10)</td>
<td>—</td>
<td>25 (51)</td>
<td>98:2</td>
</tr>
</tbody>
</table>

a) The palladium-catalyzed reactions of 18 were carried out in AcOH at 80 °C for 4 h. b) The corrected yields based on the recovered starting material are given in parentheses.

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*Chart 4*

18 → TolO₂S⁺ + TolO₂S⁻

<table>
<thead>
<tr>
<th>20a</th>
</tr>
</thead>
<tbody>
<tr>
<td>20b</td>
</tr>
</tbody>
</table>

*Chart 5*

22a → LₙPd⁺⁺⁻→ R

<table>
<thead>
<tr>
<th>23a</th>
</tr>
</thead>
<tbody>
<tr>
<td>24a</td>
</tr>
</tbody>
</table>

23b → LₙPd⁺⁺⁻→ R

<table>
<thead>
<tr>
<th>23c</th>
</tr>
</thead>
<tbody>
<tr>
<td>24b</td>
</tr>
</tbody>
</table>
because no isomerization of the unstable isomer 24b into the stable one 24a was observed under the palladium-catalyzed reaction conditions in acetic acid at 80 °C (upon treatment with Pd(PPh)4, in acetic acid at 80 °C for 4h, 19a, b (19a: 19b: 1: 19 and 69: 31) was recovered without any change of the ratio).

In conclusion, these allylic systems bearing allylic sulfones at appropriate sites undergo metallo-ene cyclizations with the allylic sulfones as enophiles upon treatment with palladium catalysts in acetic acid to give cyclohexene derivatives having allylic sulfonil groups, with extremely high diastereoselectivity.

Experimental

Infrared (IR) spectra were obtained in the indicated state with a JASCO DR-81 Fourier-transform infrared spectrometer. NMR spectra were determined in an indicated solvent with a JEOL GSX-400 (H-NMR, 400 MHz), EX-270 (1H-NMR, 270 MHz), or JNM PMX-60H (60 MHz) high resolution NMR spectrometer; chemical shifts are given in ppm from tetramethylsilane as an internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (MS) were taken on a JEOI JMS-DX303/JMA-DA5000 system. High performance liquid chromatographic data (HPLC) were obtained with a Tosoh UV-8010 CCPM (column, Tosoh TSK-gel ODS-80TM). Flash column chromatography was performed with Merck silica gel 60 (230–400 mesh). Thin layer plates dried at 140 °C for 3.5 h were used.

Dimethyl (4-Methoxybenzylidene)-2(3H)-butenone (1a)

A dry 200 ml two-necked flask equipped with a septum inlet and a magnetic stirring, containing sodium hydride (NaH) (60% oil dispersion, 799 mg, 16.6 mmol), was flushed with nitrogen, and maintained under a positive pressure of nitrogen. Anhydrous THF (100 ml) was added to the flask. A solution of dimethyl malonate (2.99 g, 22.7 mmol) in anhydrous THF (10 ml) was added to the above solution at 0 °C, and the mixture was stirred at 0 °C for 30 min. A solution of 4-acyetoxy-2-Z-butenoic acid (2.9 g, 15.1 mmol) in anhydrous THF (10 ml) was added, and the reaction mixture was further stirred at 0 °C for 2 h. The reaction solution was diluted with ether, and washed with 10% aqueous HCl, saturated aqueous NaCl, and saturated aqueous Na2SO4, and concentrated in vacuo. The residual colorless oil was isolated by column chromatography (ether-hexane: 1:4) to give 1a (2.65 g, 72% yield).

Dimethyl (4-Acetoxy-2(3H)-butenone)propanedioate (1b)

The alkylation of dimethyl malonate (3.0 g, 22.7 mmol) with 4- methoxybenzylidene-2(3H)-butenone (3.5 g, 15.1 mmol) was carried out in the same manner as described in the preparation of 1a. The crude colorless oil was subjected to column chromatography on silica gel with ether-hexane (1:4) to give 1b (2.8 g, 72% yield).

Dimethyl (4-Butenylidyne)-2(3H)-butenone (2a)

A mixture of NaH (60% oil dispersion, 541 mg, 0.90 mmol) and 1a (2.0 g, 8.2 mmol) in anhydrous THF (60 ml) was stirred at 0 °C for 30 min under a nitrogen atmosphere. A solution of (4-acyetoxy-2H-pyran-2-ylidene)-2(3H)-butenyl bromide (2.3 g, 9.0 mmol) in anhydrous THF (10 ml) was added and the reaction mixture was further stirred at 0 °C for 2 h. The reaction solution was diluted with ether, and washed with 10% aqueous HCl, saturated aqueous Nagram, and saturated aqueous Na2SO4, and concentrated in vacuo. The organic layers were combined, then dried over anhydrous Na2SO4 and concentrated in vacuo. The residual colorless oil was subjected to column chromatography (ether-hexane: 1:4) to give 2a (2.35, 72% yield).

Dimethyl (4-Butenylidyne)-2(3H)-butenone (2b)

A mixture of NaH (60% oil dispersion, 541 mg, 0.90 mmol) and 1b (2.0 g, 8.2 mmol) in anhydrous THF (60 ml) was stirred at 0 °C for 30 min under a nitrogen atmosphere. A solution of (4-acyetoxy-2H-pyran-2-ylidene)-2(3H)-butenyl bromide (2.3 g, 9.0 mmol) in anhydrous THF (10 ml) was added and the reaction mixture was further stirred at 0 °C for 2 h. The reaction solution was diluted with ether, and washed with 10% aqueous HCl, saturated aqueous Nagram, and saturated aqueous Na2SO4, and concentrated in vacuo. The organic layers were combined, then dried over anhydrous Na2SO4 and concentrated in vacuo. The residual colorless oil was subjected to column chromatography (ether-hexane: 1:4) to give 2b (2.35, 72% yield).

Dimethyl (4-Butenylidyne)-2(3H)-butenone (3a)

A mixture of NaH (60% oil dispersion, 541 mg, 0.90 mmol) and 1a (2.0 g, 8.2 mmol) in anhydrous THF (60 ml) was stirred at 0 °C for 30 min under a nitrogen atmosphere. A solution of (4-acyetoxy-2H-pyran-2-ylidene)-2(3H)-butenyl bromide (2.3 g, 9.0 mmol) in anhydrous THF (10 ml) was added and the reaction mixture was further stirred at 0 °C for 2 h. The reaction solution was diluted with ether, and washed with 10% aqueous HCl, saturated aqueous Nagram, and saturated aqueous Na2SO4, and concentrated in vacuo. The organic layers were combined, then dried over anhydrous Na2SO4 and concentrated in vacuo. The residual colorless oil was subjected to column chromatography (ether-hexane: 1:4) to give 3a (2.35, 72% yield).
butene)propane (4a). A solution of p-toluene sulfonyl chloride (67 mg, 0.38 mmol) in anhydrous THF (1 ml) was added to a solution of 3a (100 mg, 0.32 mmol) and triethylamine (Et3N) (48 mg, 0.48 mmol) in anhydrous THF (6 ml) at 0°C. The reaction mixture was stirred for 30 min, then diluted with ether, and the suspension was filtered through Celite. The filtrate was concentrated in vacuo. The residual yellow oil was subjected to preparative TLC with eluent 2:1 to 85% yield. IR νmax cm⁻¹: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfone). 1H-NMR (CDCl₃) δ: 2.00 (3H, s, CH₃), 2.40 (4H, s, CH₂(CO₂Me), 3.70 (9H, s, CH₃CO₂), 3.80-4.80 (4H, m, 2CH₃OH), 5.00-5.90 (4H, m, 2CH=CH₂), 7.20-7.80 (4H, m, C₆H₄). MS m/z: 452 (M⁺). Exact mass determination: 452.1930 (Calcd for C₂₆H₂₅O₂S: 452.1951).

7a, b.

85% yield. IR νmax cm⁻¹: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfone). 1H-NMR (CDCl₃) δ: 2.40 (3H, s, CH₃(CH₂)₂), 2.20-2.90 (4H, d, CH₂(CO₂Me)₂), 3.70 (9H, s, CH₃CO₂), 3.80-4.80 (4H, m, 2CH₃OH), 5.00-5.90 (4H, m, 2CH=CH₂), 7.20-7.80 (4H, m, C₆H₄). MS m/z: 468 (M⁺). Exact mass determination: 468.1253 (Calcd for C₂₆H₂₄O₂S: 468.2454).

8a.

93% yield. IR νmax cm⁻¹: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfone). 1H-NMR (CDCl₃) δ: 2.00 (3H, s, CH₃), 2.40 (4H, s, CH₂(CH₂)₂), 2.20-2.90 (4H, d, CH₂(CO₂Me)₂), 3.70 (9H, s, CH₃CO₂), 3.80-4.80 (4H, m, 2CH₃OH), 5.00-5.90 (4H, m, 2CH=CH₂), 7.20-7.80 (4H, m, C₆H₄). MS m/z: 452 (M⁺). Exact mass determination: 452.1930 (Calcd for C₂₆H₂₅O₂S: 452.1951).

8b.

74% yield. IR νmax cm⁻¹: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfone). 1H-NMR (CDCl₃) δ: 2.40 (3H, s, CH₃(CH₂)₂), 2.20-2.90 (4H, d, CH₂(CO₂Me)₂), 3.70 (9H, s, CH₃CO₂), 3.80-4.80 (4H, m, 2CH₃OH), 5.00-5.90 (4H, m, 2CH=CH₂), 7.20-7.80 (4H, m, C₆H₄). MS m/z: 468 (M⁺). Exact mass determination: 468.1253 (Calcd for C₂₆H₂₄O₂S: 468.2454).

Dimethyl (1-Methylcyclobutyl(cyclopropyl)methyl)imidazolium (5a) A solution of 4a (100 mg, 0.22 mmol) in anhydrous DCM (2 ml) was stirred at 125°C for 24 h and then concentrated in vacuo. The crude product was subjected to preparative TLC (ether-hexane, 3: 2) to give 5a (91 mg, 91% yield). IR νmax cm⁻¹: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). 1H-NMR (CDCl₃) δ: 2.00 (3H, s, CH₃), 2.40 (4H, s, CH₂(CH₂)₂), 2.20-2.90 (4H, m, CH₂(CO₂Me)_2), 3.60-3.80 (10H, m, CH₃CO₂), 4.50-4.70 (2H, m, CH₂CH₂), 5.35-5.60 (2H, m, CH₃CO₂), 5.50-5.80 (2H, m, CH=CH₂), 7.20-7.80 (4H, m, C₆H₄). MS m/z: 452 (M⁺). Exact mass determination: 452.1930 (Calcd for C₂₆H₂₅O₂S: 452.1951).

Dimethyl (1-(Methylcyclobutyl(4,4-dimethyl-2-oxazolidin-2-yl)oxy)-2-ethyl)propane-1-ol (10) (1H, m, CH₃), 2.20-2.90 (4H, m, CH₂(CH₂)₂), 3.60-3.80 (10H, m, CH₃CO₂), 4.50-4.70 (2H, m, CH₂CH₂), 5.35-5.60 (2H, m, CH₃CO₂), 5.50-5.80 (2H, m, CH=CH₂), 7.20-7.80 (4H, m, C₆H₄). MS m/z: 468 (M⁺). Exact mass determination: 468.1454 (Calcd for C₂₆H₂₄O₄S: 468.1454).

The thermal rearrangement of 8a, b was carried out at 115°C in the same manner as described above, to give 6a, 6b in 86 and 85% yields, respectively.
Dimethyl 4-Methylene-3-p-toluenesulfonyl-5-vinyl-1,1-cyclohexanedicarboxylate (19) A mixture of Pd(dba)$_3$ (1.3 mg, 0.005 mmol) and PPh$_3$ (4.3 mg, 0.016 mmol) in anhydrous Ac$_2$O (1 ml) was stirred at room temperature for 5 min under a nitrogen atmosphere. A solution of Sa (50 mg, 0.11 mmol) in anhydrous Ac$_2$O (1 ml) was added and the mixture was stirred at 80$^\circ$C for 4 h. The mixture was filtered through Celite and the filtrate was concentrated to dryness under reduced pressure. The residue was dissolved in dichloromethane, and the solution was washed with saturated aqueous NaHCO$_3$ and saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The crude product was subjected to preparative TLC (ether–hexane, 3:2) to give 19 (10 mg, 24% yield). The results obtained with Sa, b under other reaction conditions are listed in Table I. 1R $^{\nu \text{cm}^{-1}}$: 1740 (C=O), 1660 (C=O), 1600 (sulfinate), 1410 (sulfinate). $^1$H-NMR (CDCl$_3$) $\delta$: 2.30 (3H, s, CH$_3$), 2.20–2.90 (4H, d, CH$_2$(CO$_2$Me)$_2$), 3.70 (6H, s, CO$_2$CH$_3$Me), 3.80–4.80 (4H, m, 20CH$_2$), 5.00–5.90 (H, m, CH=CH, C=CH), 7.20–7.80 (4H, m, CH$_3$) MS m/z: 466 (M$^+$). Exact mass determination: 466.1522 (Calc for C$_{22}$H$_{24}$O$_9$S: 466.1661).

References


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