Supporting Information

Facile Syntheses of Allylic Allenethio-sulfinates and -sulfonates, and of β -Iodo- α,β -Unsaturated γ -Sultines

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¹³C NMR spectra for all new compounds (**3a**: S-2; **3b**: S-4; **6a**: S-6; **6b**: S-8; **7a**: S-10; **7b**: S-12; **7c**: S-14; **7d**: S-16; **8a**: S-18;
8b: S-20 (the first diastereoisomer), S-22 (the second diastereoisomer); **12**: S-24; **15a**: S-26; **16**: S-28)

¹H NMR spectra for all new compounds (**3a**: S-3; **3b**: S-5; **6a**: S-7; **6b**: S-9; **7a**: S-11; **7b**: S-13; **7c**: S-15; **7d**: S-17; **8a**: S-19;
8b: S-21 (the first diastereoisomer), S-23 (the second diastereoisomer); **12**: S-25; **15a**: S-27; **16**: S-29)

Experimental procedures for **3a,b**; **6a,b**; **7a-d**; **8a,b**; **12**; **15a**; **16**: S-30

Current Data Parameters
 NAME 532-silica-all
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050410
 Time 16.24
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zgdc
 TD 32768
 SOLVENT CDCl3
 NS 1321
 DS 0
 SMH 19723.865 Hz
 FIDRES 0.601925 Hz
 AQ 0.8307188 sec
 RG 5792.6
 OW 25.350 usec
 DE 9.46 usec
 TE 300.0 K
 D1 0.10000000 sec
 D11 0.10000000 sec

----- CHANNEL f1 -----
 NUC1 13C
 P1 3.00 usec
 PL1 -5.00 dB
 SF01 75.4759867 MHz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 -6.00 dB
 PL12 10.00 dB
 SF02 300.1312000 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677445 MHz
 MDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.50 cm
 CY 8.83 cm
 F1P 220.000 ppm
 F1 16602.90 Hz
 F2P -5.000 ppm
 F2 -377.34 Hz
 PPMCM 10.00000 ppm/c
 HZCM 754.67743 Hz/cm

Current Data Parameters
NAME 534-silica11
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050419
Time 12.11
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 1532
DS 0
SWH 19723.865 Hz
FIDRES 0.601925 Hz
AQ 0.8307188 sec
RG 5792.6
DW 25.350 usec
DE 9.46 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.10000000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 3.00 usec
PL1 -5.00 dB
SF01 75.4759867 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 10.00 dB
SF02 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 75.4677427 MHz
MDN EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.50 cm
CY 8.01 cm
FIP 220.000 ppm
F1 16602.90 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 10.00000 ppm/c
HZCM 754.67743 Hz/cm

Current Data Parameters
 NAME 537-silica11
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050518
 Time 12.14
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zgdc
 TD 32768
 SOLVENT CDCl3
 NS 669
 DS 0
 SMH 19723.865 Hz
 FIDRES 0.601925 Hz
 AQ 0.8307188 sec
 RG 5792.6
 DM 25.350 usec
 DE 9.46 usec
 TE 300.0 K
 D1 0.10000000 sec
 D11 0.10000000 sec

----- CHANNEL f1 -----
 NUC1 13C
 P1 3.00 usec
 PL1 -5.00 dB
 SF01 75.4759867 MHz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 -6.00 dB
 PL12 10.00 dB
 SF02 300.1312000 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677469 MHz
 MDW EM
 SS8 0
 LB 2.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.50 cm
 CY 6.34 cm
 F1P 220.000 ppm
 F1 16602.90 Hz
 F2P -5.000 ppm
 F2 -377.34 Hz
 PRNCH 10.00000 ppm/c
 HZCM 754.67749 Hz/cm

Current Data Parameters
NAME 533-56
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050419
Time 7.20
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgdc
TD 32768
SOLVENT CDC13
NS 40000
DS 0
SMH 19723.865 Hz
FIDRES 0.601925 Hz
AQ 0.8307188 sec
RG 5792.6
DM 25.350 usec
DE 9.46 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.10000000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 3.00 usec
PL1 -5.00 dB
SF01 75.4759867 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 10.00 dB
SF02 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 75.4677541 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.50 cm
CY 8.00 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCH 10.00000 ppm/c
HZCM 754.67749 Hz/cm

Current Data Parameters
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EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050519
Time 8.17
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgdc
TD 32768
SOLVENT CDC13
NS 26214
DS 0
SMH 19723.865 Hz
FIDRES 0.601925 Hz
AQ 0.8307188 sec
RG 5792.6
DM 25.350 usec
DE 9.46 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.10000000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 3.00 usec
PL1 -5.00 dB
SF01 75.4759867 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 10.00 dB
SF02 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 75.4677506 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.50 cm
CY 30.00 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 10.00000 ppm/c
HZCM 754.67749 Hz/cm

Current Data Parameters
NAME 486-s.3
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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Time 6.59
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PROBHD 5 mm Dual 13C/
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 40000
DS 0
SMH 19723.865 Hz
FIDRES 0.601925 Hz
AQ 0.8307188 sec
RG 5792.6
DW 25.350 usec
DE 9.46 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.10000000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 3.00 usec
PL1 -5.00 dB
SF01 75.4759867 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 10.00 dB
SF02 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 75.4677499 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.50 cm
CY 15.50 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 10.00000 ppm/c
HZCM 754.67749 Hz/cm

Current Data Parameters
NAME 486-i
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20041129
Time 7.12
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 40000
DS 0
SMH 19723.865 Hz
FIDRES 0.601925 Hz
AQ 0.8307188 sec
RG 5792.6
DM 25.350 usec
DE 9.46 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.10000000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 3.00 usec
PL1 -5.00 dB
SF01 75.4759867 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 10.00 dB
SF02 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 75.4677487 MHz
MDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.50 cm
CY 30.00 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -5.000 ppm
F2 -377.34 Hz
PPMCM 10.00000 ppm/c
HZCM 754.67749 Hz/cm

Current Data Parameters
 NAME 505-sil3
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
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 Time 7.52
 INSTRUM spect
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 PULPROG zgdc
 TD 32768
 SOLVENT CDC13
 NS 30532
 DS 0
 SMH 19723.865 Hz
 FIDRES 0.601925 Hz
 AQ 0.8307188 sec
 RG 5792.6
 DM 25.350 usec
 DE 9.46 usec
 TE 300.0 K
 D1 0.10000000 sec
 D11 0.10000000 sec

----- CHANNEL f1 -----
 NUC1 13C
 P1 3.00 usec
 PL1 -5.00 dB
 SF01 75.4759867 MHz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 -6.00 dB
 PL12 10.00 dB
 SF02 300.1312000 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677512 MHz
 MDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.50 cm
 CY 20.00 cm
 F1P 220.000 ppm
 F1 16602.90 Hz
 F2P -5.000 ppm
 F2 -377.34 Hz
 PPMCM 10.00000 ppm/c
 HZCM 754.67749 Hz/cm

Experimental Procedures

Preparation of the Thiosulfinates. Thiosulfinates **3a,b** and **6a,b** were prepared by the reaction of the appropriate propargylic or allylic alkoxy chlorodisulfide with 2-methyl-1,3-butadiene in the manner detailed previously for the reaction with 2,3-dimethyl-1,3-butadiene.^{2b}

Oxidation of the Allenethiosulfinates 3a-d with Sodium Metaperiodate. To a cooled (+4 °C) solution of the appropriate thiosulfinate (1 mmol) in 4 mL of acetic acid was added dropwise with stirring a solution of sodium metaperiodate (1.2 mmol) in 4 mL of water. After further stirring for 30 min the reaction mixture was kept in the refrigerator at +4 °C for 24 h (5 days for **3b**). The workup followed the published procedure.^{5b} The yields of products were 94% for **7a**, 87% for **7b** and **7c**, and 76% for **7d**. When the oxidation was performed at room temperature according to the published procedure^{5b} (using acetic acid for **3a,b,d** and aqueous dioxane/H⁺ for **3c** and at room temperature), workup led to a mixture of compounds **7** and **8** which were separated by column chromatography on silica eluting with hexane, followed by hexane/ethyl acetate (200:5). The reaction times and yields are given in Scheme 4. The 4-chloro-thiol moiety lost in the formation of **8** was discarded in the base washing of the workup.

Methyl Buta-1,2-diene-1-sulfinate (15a) was prepared according to the procedure reported for the preparation of **15b**¹⁰ and was purified by column chromatography using silica gel with chloroform as eluent.

General Procedure for the Preparation of the Sultines. To a stirred solution of the appropriate allenesulfinate (10 mmol) in 100 mL of methylene chloride at rt, was added a solution of iodine (20 mmol) in 50 mL of methyle chloride. After the appropriate time, methylene chloride solution was washed with an aqueous solution of Na₂S₂O₃ and then with water. After drying over anhydrous MgSO₄ and removal of the solvent under reduced pressure, the products were separated by column chromatography using silica gel with chloroform as eluent. All products were obtained as viscous oils.