An efficient One-Pot Approach to the Synthesis of Symmetric Trithiocarbonates from Carbon Disulfide and Alkyl Halides Using Imidazole

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General procedures for the synthesis of symmetrical trithiocarbonates from alkyl halides and carbon disulfide:

Alkyl halides (2.0 mmol) (or alkyl dihalides (1.0 mmol)) were added in one portion to a solution of imidazole (6.0 mmol) and CS₂ (6.0 mmol) in 5 mL DMSO/ H₂O (4.8/ 0.2). The color of the resulting reaction solution immediately changed from light red to yellow. Then, the solution was allowed to stir for the appropriate time (Table 2) at 45 °C in air atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, 20 ml CH₂Cl₂ was added to the mixture, and the mixture was then washed with water (2×20 ml). The organic layer was separated and then dried over anhydrous Na₂SO₄. The solvent was evaporated under the reduced pressure. The residue was purified by preparative TLC (silica gel, *eluent* *n*-hexane: EtOAc; 30:1) to afford pure product (symmetric dialkyl trithiocarbonate). In the case of entries 10 and 11, table 2 (**6j** and **6k**) the TLC *eluent* was *n*-hexane: EtOAc 4:1.

Table 2, Entry2 (**6b**): yellow oil

¹H NMR(400MHz,CDCl₃): δ = 3.0(s, 4H), 7.4 (m, 10H).

¹³C NMR (100MHz, CDCl₃): δ = 41.4, 127.9, 121.6, 129.3, 133.2, 135.0, 222.7.

Table 2, Entry5 (**6e**): pale yellow oil

Supporting Information

^1H NMR(400MHz, CDCl_3): δ = 1.01 (t, J = 7.2 Hz, 3H), 1.4 (d, J = 6.8 Hz, 12 H), 1.65-1.83 (m, 2H.), 4.21(sext, J = 6.8 Hz, 2H).

^{13}C NMR (100MHz, CDCl_3): δ = 11.4, 19.6, 23.2, 28.8, 47.9, 224.1.

Table 2, Entry6 (6f): pale yellow oil

^1H NMR(400MHz, CDCl_3): δ = 1.41(d, J = 6.8 Hz, 12 H), 4.21 (sept, J = 7.2 Hz, 2H).

^{13}C NMR (100MHz, CDCl_3): δ = 22.0, 41.6, 223.6.

Table 2, Entry7 (6g): yellow solid, M p= 64-65 °C

^{13}C NMR (100MHz, CDCl_3): δ = 14.1, 20.72, 223.3.

MS (EI, 70 eV): m/z = 57.1, 64, 71.2, 83.0, 91.2, 111.2, 123.2, 158.2, 168.1, 223.9.

Table 2, Entry4 (6h): yellow oil

^1H NMR(400 MHz, CDCl_3): δ = 3.05 (t, J = 7.8 Hz, 4 H), 3.67(t, J = 7.8 Hz, 4 H), 7.26 - 7.37(m, 10H).

^{13}C NMR (100MHz, CDCl_3): δ = 34.5, 37.9, 126.7, 128.6, 128.6, 139.6, 223.7.

MS (EI, 70 eV): m/z = 51, 65, 77, 91, 104.1, 135, 214.1, 319.1.

Table 2, Entry 9 (6i): yellow oil

Supporting Information

^1H NMR(400MHz, CDCl_3): δ = 2.1 (quin, J = 7.4Hz, 4 H), 2.79 (t, J =7.6 Hz, 4 H), 3.4 (t, J =7.4 Hz, 4H), 7.26-7.38 (m, 10H).

^{13}C NMR (100MHz, CDCl_3): δ = 29.7, 34.9, 36.1, 126.2, 129.5, 140.9, 224.1.

MS (EI, 70 eV): m/z = 65.1, 91.1, 117.2, 151.1, 195.1, 313.2, 347.3.

Table 2, Entry 10 (6j): Pale yellow oil

^1H NMR(400MHz, CDCl_3): δ = 1.32 (t, J = 7.2 Hz, 6H), 4.20 (s, 4 H), 4.26 (q, J =7.0 Hz, 4H).

^{13}C NMR (100MHz, CDCl_3): δ = 14.1, 38.9, 62.2, 167.1, 220.3.

MS (EI, 70 eV): m/z = 59.1, 87.1, 107, 119, 135, 140.1, 168, 195, 206, 237.1, 282.1.

Table 2, Entry12 (6l): yellow oil

^1H NMR(400MHz, CDCl_3): δ = 4.1 (d, J = 6.8 Hz, 4 H), 5.20(dd, J = 10.4, 0.8 Hz, 2H), 5.36(dd, J =17.2, 1.2 Hz, 2H), 5.93(m, 2H).

^{13}C NMR (100MHz, CDCl_3): δ = 39.1, 119.6, 130.7, 222.4.

Table 3, Entry 3 (8c): yellow oil

^1H NMR(400MHz, CDCl_3): δ = 2.51 (t, J = 2.0 Hz, 4 H), 3.29 (t, J =2.0 Hz, 4 H).

^{13}C NMR (100MHz, CDCl_3): δ = 29.72, 38.69, 223.32.

MS (EI, 70 eV): m/z = 54.1, 60.1, 76, 88.1, 120.1, 164.1.

Product 9: pale yellow oil

Supporting Information

^1H NMR(400MHz, CDCl_3): δ =1.3 (t, J = 7.2 Hz, 3 H), 1.41(t, J = 7.4 Hz, 3H), 3.4 (q, J = 7.4 Hz, 2 H), 4.20 (s, 2H), 4.26(q, J = 7.2 Hz, 2H).

^{13}C NMR (100MHz, CDCl_3): δ = 12.9, 14.1, 31.8, 38.4, 62.1, 167.5, 222.2.

MS (EI , 70 eV): m/z = 61, 77, 106, 120, 135, 163, 179, 195, 224.1.

Intermediate **I**: yellow oil

^1H NMR(400MHz, CDCl_3): δ = 4.64(s, 2H), 7.14(s, 1H), 7.29-7.43 (m, 5H), 7.8 (s, 1H), 8.52 (s, 1H).

^{13}C NMR (100MHz, CDCl_3): δ = 41.8, 117.7, 128.3, 128.9, 129.4, 131.5, 133.5, 135.7, 197.3.

MS (EI , 70 eV): m/z = 50, 57.1, 65.2, 76.1, 83.1, 91.2, 111.2, 123.2, 158.2, 168.1, 234.1.

Supporting Information

Supporting Information

NAME 11am UN
EXPNO 742
PROCNO 1
Date_ 20130212
Time 13.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894866 sec
RG 1620
DW 62.400 usec
DE 6.50 usec
TE 295.8 K
D1 6.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PLW 11.86359406 W
SFO1 400.2236020 MHz
S1 32768
SF 400.2200000 MHz
WVW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NAME 11am UN
EXPNO 742
PROCNO 1
Date_ 20130212
Time 13.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894866 sec
RG 1620
DW 62.400 usec
DE 6.50 usec
TE 295.8 K
D1 6.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PLW 11.86359406 W
SFO1 400.2236020 MHz
S1 32768
SF 400.2200000 MHz
WVW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Supporting Information

File: C:\MSDCHEM\3\DATA\Snapshot\Z-T-21.D
Acquired: 28 Aug 2013 19:19 using AcqMethod LOW ENERGY.M
Instrument: MSD Direct Probe
Sample Name:
Misc Info:
Vial Number: 1

Supporting Information

Supporting Information

Supporting Information

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PROCNO        1
Date_         20130526
Time          17.11
INSTRUM       spect
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PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            920
DS            0
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG            2050
DW            19.800 usec
DE            6.50 usec
TE            295.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            9.00 usec
PL1           -0.90 dB
PL1W          42.02801895 W
SFO1          100.6479784 MHz

===== CHANNEL f2 =====
CPOPRG2       waltz16
NUC2          1H
PCPD2         90.00 usec
PL2           -2.00 dB
PL12          14.16 dB
PL13          17.90 dB
PL1W          11.96359405 W
PL12W         0.28722104 W
PL13W         0.12139934 W
SFO2          400.2216009 MHz
SI            32768
SF            100.6353990 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
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Supporting Information

Supporting Information

NAME 11am UN
EXPNO 802
PROCNO 1
Date_ 20130526
Time 14.18
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 220
DS 0
SWH 25257.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PLW 42.02801895 W
SFO1 100.6479784 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 14.16 dB
PL13 17.90 dB
PLW 11.06359405 W
PL12W 0.28722104 W
PL13W 0.12139934 W
SFO2 400.2216009 MHz
S1 32768
SF 100.6353990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

NAME 11am UN
EXPNO 802
PROCNO 1
Date_ 20130526
Time 14.18
INSTRUM spect
PROBHD 5 mm TAIHO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 220
DS 0
SWH 25257.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PLW 42.02801895 W
SFO1 100.6479784 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 14.16 dB
PL13 17.90 dB
PLW 11.06359405 W
PL12W 0.28722104 W
PL13W 0.12139934 W
SFO2 400.2216009 MHz
S1 32768
SF 100.6353990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Supporting Information

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Supporting Information

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 Date_ 147
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 F11EE OC 100
 T1 50761
 SOLVENT CDCl3
 RT 400
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 FWH 25252515 Hz
 FIDRES 0.170448 Hz
 AQ 0.6482564 sec
 RG 2048
 FV 15.00 sec
 F1 650 sec
 T1 294.2 K
 F1 1.0000000 sec
 F11 0.0500000 sec
 T10 1

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 P1 0.74 sec
 PM -140 dB
 F1M 40.0015002 V
 F1C1 200.1425047 MHz

===== CHANNEL f2 =====
 (F1)EC2 val16
 NU1 120
 F (F1)2 20.00 sec
 F12 0.00 dB
 F1M2 13.28 dB
 F1M5 13.28 dB
 F12M 13.0210045 V

Supporting Information

File : C:\MSDCHEM\3\DATA\Snapshot\Z-T-10.D
Operator :
Acquired : 26 Aug 2013 19:08 using AcqMethod LOW ENERGY.M
Instrument : MSD Direct Probe
Sample Name:
Misc Info :
Vial Number: 1

Supporting Information

File: C:\MSDCHEM\3\DATA\Snapshot\IELAM(Z.T.1).D
Operator:
Acquired: 21 May 2013 16:46 using AcqMethod low energy.M
Instrument: MSD Direct Probe
Sample Name:
Misc Info:
Vial Number: 1

Supporting Information

File: C:\MSDCHEM\3\DATA\Snapshot\IELAM(ZT5).D

Operator:

Acquired: 21 May 2013 16:55 using AcqMethod low energy.M

Instrument: MSD Direct Probe

Sample Name:

Misc Info:

Vial Number: 1

Vial Number: 1

Supporting Information

File : C:\MSDCHEM\3\DATA\Snapshot\IELAM(ZT4).D
Operator :
Acquired : 21 May 2013 17:02 using AcqMethod low energy.M
Instrument : MSD Direct Probe
Sample Name :
Misc Info :
Vial Number: 1

Supporting Information

File: C:\MSDCHEM\3\DATA\Snapshot\IELAM(Z.T.8).D
Acquired: 21 May 2013 16:37 using AcqMethod low energy.M
Instrument: MSD Direct Probe
Sample Name:
Misc Info:
Vial Number: 1

Supporting Information

File: C:\MSDCHEM\3\DATA\Snapshot\IELAM(Z.T.6).D

Operator:

Acquired: 21 May 2013 16:42 using AcqMethod low energy.M

Instrument: MSD Direct Probe

Sample Name:

Misc Info:

Vial Number: 1