Supplementary Information

Behaviour of iprit carbonate analogues in solventless reactions

Fabio Aricò, Serena Evaristo, Pietro Tundo
SUPPORTING INFORMATION

$^1$H NMR, $^{13}$C NMR, GC-MS spectra and HRMS analysis of 2-(ethylcarbonate)ethyl sulfide S2

GC-MS spectrum of the reaction of several nucleophiles with 2-(methylthio)ethyl methyl carbonate 1 – Product identification 12-23 (entry 1-7, Table 2) S5

$^1$H NMR spectrum of methyl 2-(4-bromophenoxy)ethyl sulfide 12 S15

$^1$H NMR, $^{13}$C NMR, GC-MS spectra and HRMS analysis of 4-[2-(methylthio)ethoxy]benzonitrile 13 S16

$^1$H NMR spectrum of methyl 2-(naphthalen-2-yloxy)ethyl sulfide 14 S19

$^1$H NMR, $^{13}$C NMR, GC-MS spectra and HRMS analysis of 1,4-bis-[2-(methylthio)ethoxy]benzene 15 S20

$^1$H NMR, $^{13}$C NMR, GC-MS spectra of 1,4-bis-[2-(methylthio)ethoxy]benzene 16 S23

$^1$H NMR, $^{13}$C NMR, GC-MS spectra and HRMS analysis of 2,2’-[2-(methylthio)ethoxy]biphenyl 18 S25

$^1$H NMR, $^{13}$C NMR, GC-MS spectra of 2-[2-(methylthio)ethoxy]-2’-methoxybiphenyl 19 S28

GC-MS spectrum of the reaction of p-cyanophenol with several mustard carbonates 2-5 – Product identification 12-23 (entry 1-4, Table 3) S30

$^1$H NMR, $^{13}$C NMR, GC-MS spectra and HRMS analysis of 4-[2-(phenylthio)ethoxy]benzonitrile 24 S34

$^1$H NMR, $^{13}$C NMR, GC-MS spectra and HRMS analysis of 4-[3-(methylthio)propoxy]benzonitrile 25 S37

$^1$H NMR, $^{13}$C NMR, GC-MS spectra and HRMS analysis of 4-[4-(methylthiobutoxy]benzonitrile 26 S40

$^1$H NMR, $^{13}$C NMR spectra and HRMS analysis of Bis[2-(4-cyanophenoxy)ethyl]sulfide 27 S43
$^1$H NMR spectrum of Bis-(2-ethylcarbonate)ethyl sulfide 7

$^13$C NMR spectrum of Bis-(2-ethylcarbonate)ethyl sulfide 7
GC-MS spectrum of Bis-(2-ethylcarbonate)ethyl sulfide 7
HRMS analysis of Bis-(2-ethylcarbonate)ethyl sulfide 7
GC-MS spectrum of the reaction of 4-bromophenol with 2-(methylthio)ethyl methyl carbonate 1 – Product identification 12 (entry 1, Table 2)

Chemical Formula: C₇H₇BrO
Exact Mass: 185.97
Molecular Weight: 187.03

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GC-MS spectrum of the reaction of $p$-cyanophenol with 2-(methylthio)ethyl methyl carbonate 1 – Product identification 13 (entry 2, Table 2)

1-bromo-4-methoxybenzene

Chemical Formula: C$_8$H$_7$NO
Exact Mass: 133.05
Molecular Weight: 133.15

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GC-MS spectrum of the reaction of $p$-cyanophenol with 2-(methylthio)ethyl methyl carbonate 1 – Product identification 13 (entry 3, Table 2)

[Diagram showing the GC-MS spectrum with peaks labeled 1 and 1 decomposition, and 1 (residual)]

Chemical Formula: C$_8$H$_7$NO
Exact Mass: 133.05
Molecular Weight: 133.15

1-bromo-4-methoxybenzene

[Diagram showing the mass spectrum with scan 1522 (9.790 min): ES187-0.D\data.ms]

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GC-MS spectrum of the reaction of β-naphtol with 2-(methylthio)ethyl methyl carbonate 1 – Product identification 14 (entry 4, Table 2)

Chemical Formula: C₁₁H₁₀O
Exact Mass: 158.07
Molecular Weight: 158.20

peak R.T. first max last PK peak corr. corr. % of
#  min scan scan scan TY height area % max. total

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2  13.692 2159 2204 2254 BB 5924094 171629765 8.33% 4.590%
3  14.820 2387 2401 2457 BB 3639239 141678671 6.88% 3.789%
4  18.882 3056 3111 3170 VV 3 10930743 2060610972 100.00% 55.114%
5  19.740 3249 3261 3344 BB 2 1758140 102890625 4.99% 2.752%
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GC-MS spectrum of the reaction of hydroquinone with 2-(methylthio)ethyl methyl carbonate 1 – Product identification 15, 16, 17 (entry 5, Table 2)
GC-MS spectrum of the reaction of biphenyl-2,2'-dihydroxyethyl methyl carbonate – Product identification 18, 19, 20 (entry 6, Table 2)
GC-MS spectrum of the reaction of phenylsulfonyl)acetonitrile with 2-(methylthio)ethyl methyl carbonate 1 – Product identification 21, 22, 23 (entry 7, Table 2)

Chemical Formula: C_{16}H_{11}NO_{2}S
Exact Mass: 209.05
Molecular Weight: 209.26
GC-MS spectrum of the reaction of phenylsulfonyl)acetonitrile with 2-(methylthio)ethyl methyl carbonate 1

**Chemical Formula:** C_{12}H_{15}NO_{2}S_{2}

**Exact Mass:** 269.05

**Molecular Weight:** 269.38

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**Chemical Formula:** C_{14}H_{19}NO_{2}S_{3}

**Exact Mass:** 329.06

**Molecular Weight:** 329.50

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**Chemical Formula:** C_{18}H_{30}N_{2}O_{2}S_{4}

**Exact Mass:** 446.18

**Molecular Weight:** 446.40
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$^{1}H$ NMR spectrum of 4-[(methylthio)ethoxy]benzonitrile 13

$^{13}C$ NMR spectrum of 4-[(methylthio)ethoxy]benzonitrile 13
GC-MS spectrum of 4-[2-(methylthio)ethoxy]benzonitrile 13
HRMS analysis of 4-[2-(methylthio)ethoxy]benzonitrile 13
$^1$H NMR spectrum of methyl 2-(naphthalen-2-yloxy)ethyl sulfide 14

![NMR Spectrum](image)
\(^1\)H NMR spectrum of 1,4-bis-[2-(methylthio)ethoxy]benzene 15

\(^{13}\)C NMR spectrum of 1,4-bis-[2-(methylthio)ethoxy]benzene 15
GC-MS spectrum of 1,4-bis-[2-(methylthio)ethoxy]benzene 15
HRMS analysis of 1,4-bis-[2-(methylthio)ethoxy]benzene 15
$^1$H NMR spectrum of 4-[2-(methylthio)ethoxy]anisole 16

$^{13}$C NMR spectrum of 4-[2-(methylthio)ethoxy]anisole 16
GC-MS spectrum of 4-[2-(methylthio)ethoxy]anisole 16

Chemical Formula: C_{10}H_{14}O_{2}S
Exact Mass: 198.07
Molecular Weight: 198.28
$^1$H NMR spectrum of 2,2’-[2-(methylthio)ethoxy]biphenyl 18

$^{13}$C NMR spectrum of 2,2’-[2-(methylthio)ethoxy]biphenyl 18

GC-MS spectrum of 2,2’-[2-(methylthio)ethoxy]biphenyl 18
HRMS analysis of 2,2’-[2-(methylthio)ethoxy]biphenyl 18
$^1$H NMR spectrum of 2-[2-(methylthio)ethoxy]-2$'$-methoxybiphenyl 19

$^{13}$C NMR spectrum of 2-[2-(methylthio)ethoxy]-2$'$-methoxybiphenyl 19
GC-MS spectrum of 2-[(2-(methylthio)ethoxy]-2'-methoxybiphenyl 19
GC-MS spectrum of the reaction of \( p \)-cyanophenol with \( 2 \)-(phenylthio)ethyl carbonate 2 – Product identification 24 (entry 1, Table 3)

**Chemical Formula:** \( C_8H_7NO \)  
Exact Mass: 133.05  
Molecular Weight: 133.15

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GC-MS spectrum of the reaction of $p$-cyanophenol with ethyl 2-(phenylthio)ethyl carbonate 3. 

Product identification 24 (entry 2, Table 3)

Chemical Formula: $C_{15}H_{13}NOS$
Exact Mass: 255.07
Molecular Weight: 255.33

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GC-MS spectrum of the reaction of \( p \)-cyanophenol with ethyl 3-(Methylthio)propyl methyl carbonate 4 – Product identification 25 (entry 3, Table 3)

Chemical Formula: C₈H₇NO
Exact Mass: 133.05
Molecular Weight: 133.15

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S32
GC-MS spectrum of the reaction of p-cyanophenol with ethyl 4-(methylthio)butyl methyl carbonate 5 – Product identification 26 (entry 4, Table 3)

Chemical Formula: C₈H₇NO
Exact Mass: 133.05
Molecular Weight: 133.15

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GC-MS spectrum of 4-[2-(phenylthio)ethoxy]benzonitrile 24
HRMS analysis of 4-[2-(phenylthio)ethoxy]benzonitrile

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$^{13}$C NMR spectrum of 4-[3-(methylthio)propoxy]benzonitrile 25
GC-MS spectrum of 4-[3-(methylthio)propoxy]benzonitrile 25
HRMS analysis of 4-[3-(methylthio)propoxy]benzonitrile 25
$^1$H NMR spectrum of 4-[4-(methylthio)butoxy]benzonitrile 26

$^{13}$C NMR spectrum of 4-[4-(methylthio)butoxy]benzonitrile 26
GC-MS spectrum of 4-[4-(methylthio)butoxy]benzonitrile 26
HRMS analysis of 4-[4-(methylthio)butoxy]benzonitrile

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$^1$H NMR spectrum of Bis[2-(4-cyanophenoxy)ethyl]sulfide 27

$^{13}$C NMR spectrum of Bis[2-(4-cyanophenoxy)ethyl]sulfide 27
HRMS analysis of Bis[2-(4-cyanophenoxy)ethyl]sulfide

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