AN UNEXPECTED SYNTHESIS OF KETENE MONOTHIOACETALS

SUPPORTING INFORMATION

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General conditions
All reactions were carried out under an inert atmosphere. Commercial reagents were used as received without further purification. All products were purified by using silica gel (SDS, Silice 60 A. C. C. 40-63 µm) or by crystallization. Analytical TLC was carried out on Merck silica gel plates using short wave (254 nm) UV light, 1% aq. KMnO₄ solution to visualise components. NMR spectra were recorded in CDCl₃ using a Bruker AMX400 operating at 400 MHz for ¹H and 100 MHz for ¹³C. The chemical shifts are expressed in parts per million (ppm) referenced to residual chloroform. ¹H NMR data are reported as follows: δ, chemical shift; multiplicity (recorded as: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quadruplet; qt, quintuplet; ht, heptuplet; dd, double doublet; ddd, double double doublet; dddd, double double double doublet; dt, double triplet; dtt, double double triplet; dttt, triple triple triplet; m, multiplet), coupling constants (J are given in Hertz, Hz) and integration. Infrared Absorption spectra were recorded as a solution in CCl₄ with a Perkin-Elmer 1600 Fourier Transform Spectrophotometer. Mass spectra were recorded with an HP 5989B mass spectrometer via direct introduction for chemical positive ionization (CI) using ammonia as the reagent gas. Melting points were determined by Reichert microscope apparatus and were uncorrected. HRMS were performed on JEOL JMS-GcMate II, GC/MS system spectrometer.

Diethyl 2-ethoxythiocarbonylsulfanylmalonate 1

To a stirred solution of diethyl chloromalonate (5 mL, 30.9 mmol) in DMF (31 mL) was added dropwise a suspension of potassium ethylxanthogenate (5 g, 30.9 mmol) in DMF (31 mL), and stirred at room temperature overnight. After that time, the reaction mixture was diluted with EtOAc, and washed several times with H₂O and Brine. The organic layer was dried and evaporated, and the residue was purified by flash column chromatography (petrol:EtOAc 95:5), to furnish the desired xanthate as a yellow oil (8.28 g, 96%).

IR (CCl₄) νmax/cm⁻¹ 1746 (CO), 1238 (O-CS), 1049 (C=S).
¹H-NMR (CDCl₃) δ 1.30 (t, J=7.2 Hz, 6 H, 2 CH₃), 1.42 (t, J=7.2 Hz, 3 H, CH₃), 4.27 (q, J=7.2 Hz, 4 H, 2 OCH₂), 4.64 (q, J=7.2 Hz, 2 H, OCH₂ xanthate), 5.29 (s, 1 H, CHS).
¹³C-NMR (CDCl₃) δ 13.3 (CH₃), 13.7 (2 CH₃), 56.0 (CHS), 62.6 (2 OCH₂), 70.8 (OCH₂ xanthate), 164.8 (2 CO), 209.8 (CS).
MS (CI) m/z 281 (MH⁺), 298 (MNH₄⁺).
HRMS calculated for C₁₀H₁₆O₅S₂ 280.0439 found 280.0444.

Optimised method for the C-alkylation of xanthate 1
To a cooled (0 ºC) solution of xanthate 1 (1 equiv.) in acetone (1 mL/mmol) was added the corresponding alkyl halide (5 equiv.) and K₂CO₃ (1.2 equiv.) and stirred at that temperature for 1 h. After that time, the reaction mixture was filtrated and concentrated. The residue was purified by flash column chromatography.
**General methods for the synthesis of the ketene monothioacetals**

Method A. To a solution of xanthate (1 equiv.) in acetone (2 mL/mmol) was added K$_2$CO$_3$ (1.5 equiv.) and stirred for 30 min (except for compound 17 that required 15 h). Then it was added the corresponding alkyl halide (1.2 equiv.) and stirred for a further 30 min. After that time, the reaction mixture was filtered and concentrated, and the residue was purified by flash column chromatography.

Method B. To a cooled (0 ºC) solution of xanthate (1 equiv.) in THF (2 mL/mmol) was added NaH (1.5 equiv.) and stirred for 15 min. at room temperature. Then it was added the corresponding alkyl halide (1.2 equiv.) and stirred for a further 30 min. After that time, the reaction was quenched by addition of saturated aqueous NH$_4$Cl solution, and it was extracted with EtOAc. The organic extracts were dried and evaporated, and the obtained residue was purified by flash column chromatography.

Method C. To a solution of xanthate (1 equiv.) in EtOH (2 mL/mmol) was added finely powdered KOH (1.1 equiv.) and heated to reflux temperature for 1 h. Then it was cooled down and it was added the corresponding alkyl halide (1.1 equiv.) and stirred for a further 30 min. After that time, the reaction was quenched by addition of saturated aqueous NH$_4$Cl solution, and it was extracted with EtOAc. The organic extracts were dried and evaporated, and the obtained residue was purified by flash column chromatography.

**Diethyl 2-ethoxythiocarbonylsulfanyl-2-methylmalonate 2a**

Yellow oil, petrol:EtOAc 9:1.

IR (CCl$_4$) $\nu_{\text{max}}$/cm$^{-1}$ 1742 (CO), 1255 (O-CS), 1027 (C=S).

$^1$H-NMR (CDCl$_3$) $\delta$ 1.28 (t, $J$=7.2 Hz, 6 H, 2 CH$_3$), 1.39 (t, $J$=7.2 Hz, 3 H, CH$_3$ xanthate), 1.95 (s, 3 H, CH$_3$), 4.24 (q, $J$=7.2 Hz, 4 H, 2 OCH$_2$), 4.60 (q, $J$=7.2 Hz, 2 H, OCH$_2$ xanthate).

$^{13}$C-NMR (CDCl$_3$) $\delta$ 12.9 (CH$_3$ xanthate), 13.7 (2 CH$_3$), 22.7 (CH$_3$), 62.4 (2 OCH$_2$), 69.9 (OCH$_2$ xanthate), 167.3 (CO), 209.0 (CS).

MS (Cl) m/z 295 (MH$^+$), 311 (MNH$_4^+$).

**Diethyl 2-benzyl-2-ethoxythiocarbonylsulfanylmalonate 2b**

Yellow oil, petrol:EtOAc 9:1.

IR (CCl$_4$) $\nu_{\text{max}}$/cm$^{-1}$ 1740 (CO), 1255 (O-CS), 1029 (C=S).

$^1$H-NMR (CDCl$_3$) $\delta$ 1.22 (t, $J$=7.2 Hz, 6 H, 2 CH$_3$), 1.41 (t, $J$=7.2 Hz, 3 H, CH$_3$ xanthate), 3.68 (s, 2 H, CH$_2$Ph), 4.19 (q, $J$=7.2 Hz, 4 H, 2 OCH$_2$), 4.60 (q, $J$=7.2 Hz, 2 H, OCH$_2$ xanthate), 7.15-7.35 (m, 5 H, ArH).

$^{13}$C-NMR (CDCl$_3$) $\delta$ 13.1 (CH$_3$), 13.7 (2 CH$_3$), 40.2 (CH$_2$Ph), 62.6 (2 OCH$_2$), 68.1 (C), 70.0 (OCH$_2$ xanthate), 127.3 (CH Ar), 128.0 (CH Ar), 130.4 (CH Ar), 134.6 (C-ipso), 166.4 (2 CO), 209.2 (CS).

MS (Cl) m/z 370 (MH$^+$), 387 (MNH$_4^+$).

**Diethyl 2-(1-ethoxy-1-methylsulfanylmethylene)malonate 3a**

Yellow oil, petrol:EtOAc 9:1, method A.

IR (CCl$_4$) $\nu_{\text{max}}$/cm$^{-1}$ 1724 (CO), 1563 (C=C).

$^1$H-NMR (CDCl$_3$) $\delta$ 1.20 (bm, 6 H, 2 CH$_3$ ester), 1.27 (t, $J$=7 Hz, 3 H, CH$_3$ acetal), 2.22 (s, 3 H, SCH$_3$), 4.04 (q, $J$=7.2 Hz, 2 H, OCH$_2$ acetal), 4.20 (bm, 4 H, 2 OCH$_2$ ester).
$^{13}$C-NMR (CDCl$_3$) δ 13.4, 13.9 and 14.7 (2 CH$_3$ ester, CH$_3$ acetal and SCH$_3$), 60.7 and 60.9 (2 OCH$_2$ ester), 71.0 (OCH$_2$ acetal), 111.3 (C=), 164.4 and 164.5 (2 CO), 172.9 (C=).

**MS** (Cl) m/z 263 (MH$^+$).

**HRMS** calculated for C$_{18}$H$_{11}$O$_5$S 262.0875 found 262.0878.

![Diethyl 2-(1-benzylsulfanyl-1-ethoxymethylene)malonate 3b](image)

Yellow oil, petrol:EtOAc 9:1, method A.

**IR** (CCl$_4$) $\nu_{\text{max}}$/cm$^{-1}$ 1725 (CO), 1563 (C=C). **$^1$H-NMR** (CDCl$_3$) δ 1.32 (bm, 6 H, 2 CH$_3$), 1.32 (t, $J$ = 7 Hz, 3 H, CH$_3$), 4.04 (s, 2 H, SCH$_2$), 4.13 (q, $J$ = 7.2 Hz, 2 H, OCH$_2$), 4.25 (bm, 4 H, 2 OCH$_2$), 7.20-7.40 (m, 5 H, ArH).

$^{13}$C-NMR (CDCl$_3$) δ 13.9 (2 CH$_3$), 14.7 (CH$_3$), 35.4 (SCH$_2$), 60.8 (OCH$_2$ ester), 70.8 (OCH$_2$ acetal), 111.6 (C=), 127.3, 128.4 and 128.7 (CH Ar), 136.2 (C Ar), 164.3 (CO), 164.6 (CO), 171.1 (C=).

**MS** (Cl) m/z 339 (MH$^+$).

**HRMS** calculated for C$_{17}$H$_{26}$O$_5$S 338.1188 found 338.1187.

![Diethyl 2-[1-ethoxy-1-(2-oxo-2-phenylethylsulfanyl)methylene]malonate 3c](image)

Yellow oil, petrol:EtOAc 8:2, method A.

**IR** (CCl$_4$) $\nu_{\text{max}}$/cm$^{-1}$ 1738 (CO ester), 1693 (CO ketone), 1558 (C=C). **$^1$H-NMR** (CDCl$_3$) δ 1.22 (t, $J$ = 7 Hz, 3 H, CH$_3$), 1.26 (t, $J$ = 7.4 Hz, 3 H, CH$_3$), 1.30 (t, $J$ = 7.4 Hz, 3 H, CH$_3$), 4.12 (q, $J$ = 6.8 Hz, 2 H, OCH$_2$ acetal), 4.16-4.28 (m, 4 H, 2 OCH$_2$ ester), 4.27 (s, 2 H, SCH$_2$), 7.49 (t, $J$ = 7.6 Hz, 2 H, ArH), 7.60 (t, $J$ = 6.8 Hz, 1 H, ArH), 7.96 (d, $J$ = 8 Hz, 2 H, ArH).

$^{13}$C-NMR (CDCl$_3$) δ 14.0 (2 CH$_3$ ester), 14.4 (CH$_3$ acetal), 59.0 (SCH$_2$), 60.7 (OCH$_2$ ester), 61.0 (OCH$_2$ ester), 62.5 (OCH$_2$ acetal), 100.0 (C=), 125.0, 129.0 and 129.7 (CH Ar), 133.7 (C Ar), 164.0 (2 CO ester), 178.8 (C=), 194.2 (CO ketone).

**MS** (Cl) m/z 321 (MH$^+$-OEt).

**HRMS** calculated for C$_{18}$H$_{22}$O$_6$S 366.1437 found 366.1440.

![Diethyl 2-[1-ethoxy-1-(prop-2-ynylsulfanyl)methylene]malonate 3d](image)

Yellow oil, petrol:EtOAc 9:1, method A.

**IR** (CCl$_4$) $\nu_{\text{max}}$/cm$^{-1}$ 3400 (C-H), 1743 (CO), 1552 (C=C). **$^1$H-NMR** (CDCl$_3$) δ 1.28 (t, $J$ = 7 Hz, 3 H, CH$_3$), 1.31 (t, $J$ = 7 Hz, 3 H, CH$_3$), 1.39 (t, $J$ = 7 Hz, 3 H, CH$_3$), 2.30 (t, $J$ = 2.8 Hz, 1 H, CH), 3.59 (d, $J$ = 2.8 Hz, 2 H, SCH$_2$), 4.21 (q, $J$ = 7 Hz, 2 H, OCH$_2$), 4.20-4.35 (m, 4 H, 2 OCH$_2$).

$^{13}$C-NMR (CDCl$_3$) δ 13.9 (CH$_3$), 14.1 (CH$_3$), 14.9 (CH$_3$), 19.0 (SCH$_2$), 61.1 (OCH$_2$ ester), 61.4 (OCH$_2$ ester), 71.88 (CH), 71.92 (OCH$_2$ acetal), 90.0 (C alkyne), 111.6 (C=), 164.4 (CO), 164.7 (CO), 170.6 (C=).
Yellow oil, petrol:EtOAc 8:2, method A.

**IR** (CCl₄) νmax/cm⁻¹: 1718 (CO), 1566 (C=C).

**¹H-NMR** (CDCl₃) δ 1.33 (t, J= 7.4 Hz, 3 H, CH₃), 1.36 (t, J= 7.2 Hz, 3 H, CH₃), 1.38 (t, J= 7 Hz, 3 H, CH₃), 3.56 (s, 2 H, CH₂), 3.73 (s, 3 H, OCH₃), 4.19 (q, J= 7.2 Hz, 2 H, OCH₂), 4.28 (q, J= 7 Hz, 2 H, OCH₂), 4.30 (q, J= 7.2 Hz, 2 H, OCH₂), 4.82 (q, 9.6 Hz, 2 H, OCH₂).

**¹³C-NMR** (CDCl₃) δ 14.0 (CH₃ ester), 14.1 (CH₃ ester), 14.8 (CH₃ acetal), 32.5 (SCH₂), 4.30 (q, J= 7 Hz, 2 H, OCH₂). 32.6 (OCH₃), 61.0 (OCH₂), 61.4 (OCH₂), 71.8 (OCH₂ acetal), 110.3 (C=), 164.6 (CO), 164.8 (CO), 169.2 (CO), 170.7 (C=).

**MS** (Cl) m/z 287 (MH⁺), 304 (MNH₄⁺).

**HRMS** calculated for C₁₃H₁₀O₅S 286.0875 found 286.0863.

**Diethyl 2-[1-ethoxy-1-(2-methoxycarbonylmethylsulfanyl)methylene]malonate 3e**

![Chemical structure of Diethyl 2-[1-ethoxy-1-(2-methoxycarbonylmethylsulfanyl)methylene]malonate 3e]

To a stirred solution of ethyl 2-chloro-3-oxobutirate (10 mL, 72.3 mmol) in DMF (72 mL) was added dropwise a suspension of potassium ethylxanthogenate (11.6 g, 72.3 mmol) in DMF (72 mL), and stirred at room temperature overnight. After that time, the reaction mixture was diluted with EtOAc and washed several times with H₂O and Brine. The organic layer was dried and evaporated, and the residue was purified by flash column chromatography (petrol:EtOAc 99:1), to furnish the desired xanthate as a yellow oil (6.60 g, 37%).

**IR** (CCl₄) νmax/cm⁻¹: 1729 (CO ester), 1636 (CO enol), 1228 (O-CS), 1045 (C=S).

**¹H-NMR** (CDCl₃) δ 1.29 (t, J= 7 Hz, 6 H, 2 CH₃ ester), 1.37 (t, J= 7 Hz, 3 H, CH₃ acetal), 2.15 (qn, J= 6.4 Hz, 2 H, CH₂), 2.99 (t, J= 7 Hz, 2 H, CH₂), 3.70 (t, J= 6.2 Hz, 2 H, CH₂), 4.16 (q, J= 7.2 Hz, 2 H, OCH₂ acetal), 4.24 (q, J= 7 Hz, 4 H, 2 OCH₂ ester).

**HRMS** calculated for C₁₃H₂₀O₅S 320.0930 found 320.0928.

**Diethyl 2-[1-(3-chloropropylsulfanyl)-1-ethoxymethylene]malonate 3f**

![Chemical structure of Diethyl 2-[1-(3-chloropropylsulfanyl)-1-ethoxymethylene]malonate 3f]

**Ethyl (E)-2-ethoxythiocarbonylsulfanyl-3-hydroxy-but-2-enoate 9**

![Chemical structure of Ethyl (E)-2-ethoxythiocarbonylsulfanyl-3-hydroxy-but-2-enoate 9]
Ethyl 2-(1-ethoxy-1-methylsulfanyl)methylene)-3-oxobutyrate

Yellow oil, petrol:EtOAc 8:2, 2 isomers A:B 6:1, method A.
IR (CCl₄) ν max/cm⁻¹ 1723 (CO), 1582 (C=S).
¹H-NMR (CDCl₃) δ 1.21 (t, J = 7.2 Hz, 0.43 H, CH₃ ester isomer B), 1.26 (t, J = 7.2 Hz, 2.57 H, CH₃ ester isomer A), 1.31 (t, J = 7.2 Hz, 2.57 H, CH₃ acetal isomer A), 1.36 (t, J = 7.2 Hz, 0.43 H, CH₃ acetal isomer B), 2.14 (s, 0.43 H, SCH₃ isomer B), 2.23 (s, 2.57 H, SCH₃ isomer A), 2.25 (s, 2.57 H, CH₃ acetyl isomer A), 2.45 (s, 2.57 H, CH₃ acetyl isomer B), 4.05 (q, J = 7.2 Hz, 2 H, OCH₂ acetyl), 4.21 (q, J = 7.2 Hz, 2 H, OCH₂ ester).
¹³C-NMR (CDCl₃) δ 13.7 (SCH₃ isomer A), 14.0 (CH₃ ester isomer A), 14.8 (CH₃ ester isomer B), 15.0 (CH₃ acetal isomer B), 23.8 (CH₃ acetyl isomer B), 29.9 (CH₃ acetyl isomer A), 60.8 (OCH₂ ester isomer B), 61.0 (OCH₂ ester isomer A), 71.5 (OCH₂ acetal isomer A), 72.6 (OCH₂ acetal isomer B), 100.8 (C= isomer B), 119.7 (C= isomer A), 159.8 (CO ester isomer A), 160.2 (CO ester isomer B), 165.9 (C= isomer A), 167.2 (C= isomer B), 194.0 (CO isomer B), 195.1 (CO isomer A).
MS (Cl) m/z 233 (MH⁺).
HRMS calculated for C₁₀H₁₆O₄S 232.0769 found 232.0774.

Dithiocarbonic acid O-ethyl ester S-{1-cyano-1-phenylmethyl} ester

To a solution of mandelonitrile (3 mL, 22.5 mmol) in CH₂Cl₂ (17 mL) cooled to 0 ºC was added carefully PCl₅ (5.63 g, 27.0 mmol) and stirred at room temperature for 1 h. After that time the reaction mixture was concentrated, the residue was redissolved in acetone (113 mL) and cooled to 0 ºC. Potassium ethylxanthenate (4.69 g, 29.3 mmol) was added, and the reaction mixture was stirred at room temperature for 2 h. Then, it was concentrated, the residue redissolved in Et₂O, and it was washed three times with H₂O. The organic phase was dried and evaporated, and the residue was purified by flash column chromatography (petrol:EtOAc 98:2), obtaining the desired xanthate as a yellow oil (3.76 g, 71%).
IR (CCl₄) ν max/cm⁻¹ 2361 (CN), 1242 (O-CS), 1047 (C=S).
¹H-NMR (CDCl₃) δ 1.48 (t, J = 7.2 Hz, 3 H, CH₃), 4.65-4.79 (m, 2 H, OCH₂), 5.66 (s, 1 H, CH), 7.30-7.60 (m, 5 H, Ar-H).
¹³C-NMR (CDCl₃) δ 13.5 (CH₃), 41.7 (CH), 71.2 (OCH₂), 117.1 (CN), 127.9, 129.2 and 129.4 (CH Ar), 129.8 (C Ar), 208.4 (CS).
MS m/z (Cl) 238 (MH⁺).
HRMS calculated for C₁₁H₁₁NOS₂ 237.0282 found 237.0282.

3-Ethoxy-3-methylsulfanyl-2-phenylacrylonitrile

Yellow oil, petrol:EtOAc 9:1, 2 isomers A:B 13:1, method B.
IR (CCl₄) ν max/cm⁻¹ 2212 (CN), 1555 (C=C).
¹H-NMR (CDCl₃) δ 1.26 (t, J = 7 Hz, 2.79 H, CH₃ isomer A), 1.44 (t, J = 7.2 Hz, 0.21 H, CH₃ isomer B), 2.20 (s, 0.21 H, SCH₃ isomer B), 2.40 (s, 2.79 H, SCH₃ isomer A), 4.11 (q, J = 7 Hz, 1.86 H, OCH₂ isomer A), 4.30 (q, J = 7 Hz, 0.14 H, OCH₂ isomer B), 7.25 (d, J = 7 Hz, 1 H, ArH), 7.33 (t, J = 7.6 Hz, 2 H, ArH), 7.61 (d, J = 7.6 Hz, 2 H, ArH).
¹³C-NMR (CDCl₃) δ 14.0 (CH₃ isomer B), 14.7 (CH₃ isomer A), 15.6 (SCH₃), 68.7 (OCH₂ isomer A), 69.9 (OCH₂ isomer B), 97.3 (C= isomer B), 100.2 (C= isomer A), ...
118.6 (CN), 127.6, 127.7 and 128.1 (CH Ar), 131.6 (C Ar), 166.8 (C= isomer A), 169.4 (C= isomer B).

**MS (Cl) m/z** 220 (MH⁺), 237 (MNH₄⁺).

![PhCN BuS OEt](image)

**3-Benzylsulfanyl-3-ethoxy-2-phenylacrylonitrile 12b**

Yellow oil, petrol:EtOAc 95:5, 2 isomers A:B 7:1, method C.

**IR** (CCl₄) ν_max/cm⁻¹ 2212 (CN), 1554 (C=C).

**¹H-NMR** (CDCl₃) δ 1.23 (t, J= 7 Hz, 2.625 H, CH₃ isomer A), 1.45 (t, J= 7 Hz, 0.375 H, CH₃ isomer B), 3.90 (s, 0.25 H, SCH₂ isomer B), 4.08 (q, J= 7.2 Hz, 1.75 H, OCH₂ isomer A), 4.13 (s, 1.75 H, SCH₂ isomer A), 4.35 (q, J= 7.2 Hz, 0.25 H, OCH₂ isomer B), 7.20-7.60 (m, 5 H, ArH).

**¹³C-NMR** (CDCl₃) δ 14.6 (CH₃ isomer A), 14.7 (CH₃ isomer B), 36.0 (SCH₂ isomer B), 38.2 (SCH₂ isomer A), 68.2 (OCH₂ isomer A), 69.3 (OCH₂ isomer B), 99.4 (C= isomer B), 103.0 (C= isomer A), 127.5, 127.7, 127.8, 128.06, 128.12, 128.3, 128.4, 128.6, 128.85, 128.92, 129.0 and 129.1 (CH Ar), 130.9, 131.4, 131.5 and 136.0 (C Ar), 167.1 and 167.4 (C=).

**MS (Cl) m/z** 296 (MH⁺), 313 (MNH₄⁺).

**HRMS** calculated for C₁₈H₁₇NOS 295.1031 found 295.1030.

![PhCN BuS OEt](image)

**3-Ethoxy-3-(2-oxo-2-phenylethylsulfanyl)-2-phenylacrylonitrile 12c**

Yellow oil, petrol:EtOAc 9:1, 2 isomers A:B 2:1, method B.

**IR** (CCl₄) ν_max/cm⁻¹ 2256 (CN), 1686 (CO), 1601 (C=C).

**¹H-NMR** (CDCl₃) δ 0.88 (t, J= 7 Hz, 1 H, CH₃ isomer B), 1.25 (t, J= 7 Hz, 2 H, CH₃ isomer A), 4.12 (q, J= 7.2 Hz, 0.67 H, OCH₂ isomer B), 4.17 (q, J= 7.2 Hz, 1.33 H, OCH₂ isomer A), 4.20 (s, 0.67 H, SCH₂ isomer B), 4.38 (s, 1.33 H, SCH₂ isomer A), 7.30-8.00 (m, 5 H, ArH).

**¹³C-NMR** (CDCl₃) δ 13.2 (CH₃), 15.0 (CH₃), 28.5 (SCH₂), 29.7 (SCH₂), 69.4 (OCH₂), 70.9 (OCH₂), 100.0 (C=), 126.2, 128.1, 128.3, 128.4, 128.5, 128.57, 128.58, 128.6, 128.8, 128.9, 129.2 and 129.6 (CH Ar), 139.96 and 139.99 (C Ar), 196.5 (CO).

**MS (Cl) m/z** 324 (MH⁺), 341 (MNH₄⁺).

**HRMS** calculated for C₁₉H₁₇NO₂S 323.0980 found 323.0982.

![PhCN BuS OEt](image)

**3-Ethoxy-3-[2-oxo-2-(4-fluorophenyl)ethylsulfanyl]-2-phenylacrylonitrile 12d**

Yellow oil, petrol:EtOAc 9:1, 2 isomers A:B 7:1, method B.

**IR** (CCl₄) ν_max/cm⁻¹ 2256 (CN), 1683 (CO), 1600 (C=).

**¹H-NMR** (CDCl₃) δ 1.26 (t, J= 7 Hz, 2.625 H, CH₃ isomer A), 1.38 (t, J= 7 Hz, 0.375 H, CH₃ isomer B), 3.95 (s, 0.25 H, SCH₂ isomer B), 4.12 (q, J= 7 Hz, 0.25 H, OCH₂ isomer B), 4.17 (q, J= 7 Hz, 1.75 H, OCH₂ isomer A), 4.33 (s, 1.75 H, SCH₂ isomer A), 7.20-8.05 (m, 5 H, ArH).
\(1^3\text{C-NMR} \ (\text{CDCl}_3) \ \delta \ 14.9 \ (\text{CH}_3), \ 15.0 \ (\text{CH}_3), \ 29.7 \ (\text{SCH}_2), \ 70.9 \ (\text{OCH}_2), \ 98.5 \ (\text{C}=), \ 116.1 \ (\text{CN}), \ 116.3 \ (\text{CN}), \ 128.3, \ 128.5, \ 128.6, \ 128.7, \ 129.2 \ and \ 129.6 \ (\text{CH Ar}), \ 131.1 \ (d, \ J=9.6 \ Hz, \ \text{CH Ar}), \ 131.2 \ (d, \ J=9.7 \ Hz, \ \text{CH Ar}), \ 143.9 \ (d, \ J=70 \ Hz, \ \text{C-F}), \ 144.8 \ (d, \ J=77 \ Hz, \ \text{C-F}), \ 204.8 \ (\text{CO}).
\)

**MS** \( (\text{Cl}) \ m/z \ 342 \ (\text{MH}^+), \ 359 \ (\text{MNH}_4^+). \)

![3-Cyanomethylsulfonyl-3-ethoxy-2-phenylacrylonitrile 12e](image)

Dark yellow oil, petrol:EtOAc 9:1, 2 isomers A:B 9:1, method B.

**IR** \( (\text{CCl}_4) \ \nu_{\text{max}}/\text{cm}^{-1} \ 2213 \ (\text{CN}), \ 1559 \ (\text{C}=). \)

\(1^1\text{H-NMR} \ (\text{CDCl}_3) \ \delta \ 1.35 \ (t, \ J=7 \ Hz, \ 3 \ H, \ \text{CH}_3), \ 3.48 \ (s, \ 0.2 \ H, \ \text{SCH}_2 \ \text{isomer B}), \ 7.20-7.70 \ (m, \ 5 \ H, \ \text{ArH}). \)

\(1^3\text{C-NMR} \ (\text{CDCl}_3) \ \delta \ 14.8 \ (\text{CH}_3 \ \text{isomer A}), \ 14.9 \ (\text{CH}_3 \ \text{isomer B}), \ 16.3 \ (\text{SCH}_2 \ \text{isomer B}), \ 18.1 \ (\text{SCH}_2 \ \text{isomer A}), \ 70.3 \ (\text{OCH}_2 \ \text{isomer A}), \ 71.9 \ (\text{OCH}_2 \ \text{isomer B}), \ 99.8 \ (\text{C=} \ \text{isomer B}), \ 104.2 \ (\text{C=} \ \text{isomer A}), \ 115.4 \ (\text{CN}), \ 117.8 \ (\text{CN}), \ 128.3, \ 128.6, \ 128.9, \ 129.1 \ and \ 129.6 \ (\text{CH Ar}), \ 130.8 \ (\text{C Ar}), \ 161.3 \ (\text{C}=). \)

**MS** \( (\text{Cl}) \ m/z \ 245 \ (\text{MH}^+), \ 262 \ (\text{MNH}_4^+). \)

**HRMS** calculated for \(C_{13}H_{12}N_2OS \ 244.0670 \) found 244.0668.

![3-Ethoxy-2-phenyl-3-(prop-2-ynylsulfanyl)acrylonitrile 12f](image)

Yellow oil, petrol:EtOAc 95:5, 2 isomers A:B 13:1, method B.

**IR** \( (\text{CCl}_4) \ \nu_{\text{max}}/\text{cm}^{-1} \ 3311 \ (\text{C-H}), \ 2213 \ (\text{CN}), \ 1554 \ (\text{C}=). \)

\(1^1\text{H-NMR} \ (\text{CDCl}_3) \ \delta \ 1.49 \ (t, \ J=7 \ Hz, \ 0.21 \ H, \ \text{CH}_3 \ \text{isomer A}), \ 2.35 \ (t, \ J=2.6 \ Hz, \ 1 \ H, \ \text{CH}), \ 3.44 \ (d, \ J=2.8 \ Hz, \ 0.14 \ H, \ \text{SCH}_2 \ \text{isomer B}), \ 3.66 \ (d, \ J=2.8 \ Hz, \ 1.86 \ H, \ \text{SCH}_2 \ \text{isomer A}), \ 4.22 \ (q, \ J=7.2 \ Hz, \ 2 \ H, \ \text{OCH}_2), \ 7.32 \ (d, \ J=7.2 \ Hz, \ 1 \ H, \ \text{ArH}), \ 7.38 \ (t, \ J=7.4 \ Hz, \ 2 \ H, \ \text{ArH}), \ 7.66 \ (t, \ J=7.2 \ Hz, \ 2 \ H, \ \text{ArH}). \)

\(1^3\text{C-NMR} \ (\text{CDCl}_3) \ \delta \ 13.2 \ (\text{CH}_3), \ 14.9 \ (\text{SCH}_2), \ 70.4 \ (\text{OCH}_2), \ 80.9 \ (\text{CH}), \ 92.5 \ (\text{C alkyn}), \ 117.7 \ (\text{CN}), \ 126.5, \ 128.5 \ and \ 128.9 \ (\text{CH Ar}), \ 136.7 \ (\text{C Ar}). \)

**Methyl 2-(ethoxythiocarbonylsulfanyl)phenylacetate 13**

To a solution of methyl mandelate (3.32 g, 20.0 mmol) in \(\text{CH}_2\text{Cl}_2\) (15 mL) cooled to 0 °C was added carefully \(\text{PCl}_5\) (5.0 g, 24.0 mmol) and stirred at room temperature for 2 h. After that time the reaction mixture was concentrated, the residue was redissolved in \(\text{EtOH}\) (80 mL) and cooled to 0 °C. Potassium ethylxanthogenate (3.85 g, 24.0 mmol) was added, and the reaction mixture was stirred at room temperature for 4 h. Then, it was concentrated, the residue redissolved in \(\text{Et}_2\text{O}\) and it was washed three times with \(\text{H}_2\text{O}\). The organic phase was dried and evaporated, and the residue was purified by flash column chromatography (petrol:EtOAc 95:5), obtaining the desired xanthate as a yellow oil (3.10 g, 57%).

**IR** \( (\text{CCl}_4) \ \nu_{\text{max}}/\text{cm}^{-1} \ 1746 \ (\text{CO}), \ 1226 \ (\text{O-CS}), \ 1054 \ (\text{C}=S). \)

\(1^1\text{H-NMR} \ (\text{CDCl}_3) \ \delta \ 1.40 \ (t, \ J=7 \ Hz, \ 3 \ H, \ \text{CH}_3 \ \text{xanthate}), \ 3.75 \ (s, \ 3 \ H, \ \text{OCH}_3), \ 4.58-4.68 \ (m, \ 2 \ H, \ \text{OCH}_2), \ 8.05 \ (s, \ 1 \ H, \ \text{CH}), \ 7.30-7.45 \ (m, \ 5 \ H, \ \text{ArH}). \)
**13C-NMR** (CDCl$_3$) $\delta$ 13.5 (CH$_3$ xanthate), 53.0 (CH), 56.8 (OCH$_3$), 70.2 (OCH$_2$), 128.5 (CH Ar), 128.7 (CH Ar), 128.9 (CH Ar), 133.1 (C Ar), 169.7 (CO), 211.5 (CS).

**MS** (Cl) $m/z$ 271 (MH$^+$), 288 (MNH$_4^+$).

**HRMS** calculated for C$_{12}$H$_{18}$O$_3$S $270.0385$ found $270.0384$.

![Methyl 3-ethoxy-3-methylsulfanyl-2-phenylacrylate 14a](Image)

Yellow oil, petrol:EtOAc 98:2, 2 isomers A:B 2:1, method B.

**IR** (CCl$_4$) $\nu_{max}$/cm$^{-1}$ 1726 and 1751 (CO), 1544 (C=C).

**1H-NMR** (CDCl$_3$) $\delta$ 1.07 (t, $J=7$ Hz, 2 H, CH$_3$ isomer A), 1.48 (t, $J=7$ Hz, 1 H, CH$_3$ isomer B), 2.21 (s, 1 H, SCH$_3$ isomer B), 2.35 (s, 2 H, SCH$_3$ isomer A), 3.68 (q, $J=7.2$ Hz, 1.33 H, OCH$_2$ isomer A), 3.74 (s, 1 H, OCH$_3$ isomer B), 3.76 (s, 2 H, OCH$_3$ isomer A), 4.21 (q, $J=7$ Hz, 0.67 H, OCH$_2$ isomer B), 7.20-7.50 (m, 5 H, ArH).

**13C-NMR** (CDCl$_3$) $\delta$ 13.9 (SCH$_3$ isomer B), 14.0 (SCH$_3$ isomer A), 14.8 (CH$_3$ isomer A), 15.1 (CH$_3$ isomer B), 51.8 (OCH$_3$ isomer B), 51.9 (OCH$_3$ isomer A), 69.6 (OCH$_2$ isomer A), 69.8 (OCH$_2$ isomer B), 117.9 (C= isomer A), 118.8 (C= isomer B), 127.1, 127.7, 127.9, 128.2, 130.15 and 130.22 (CH Ar), 134.9 and 135.6 (C Ar), 164.2, 165.9, 167.0 and 168.4 (CO and C=).

**HRMS** calculated for C$_{13}$H$_{16}$O$_3$S $252.0820$ found $252.0824$.

![Methyl 3-ethoxy-3-(2-oxo-2-phenylethylsulfanyl)-2-phenylacrylate 14b](Image)

Yellow oil, petrol:EtOAc 85:15, 2 isomers A:B 2:1, method B.

**1H-NMR** (CDCl$_3$) $\delta$ 0.90 (t, $J=7.2$ Hz, 2 H, CH$_3$ isomer A), 1.34 (t, $J=7$ Hz, 1 H, CH$_3$ isomer B), 3.58 (q, $J=7.2$ Hz, 1.33 H, OCH$_2$ isomer A), 3.65 (s, 2 H, OCH$_3$ isomer A), 3.65 (s, 2 H, OCH$_3$ isomer B), 4.09 (s, 0.67 H, SCH$_2$ isomer B), 4.16 (q, $J=7.2$ Hz, 0.67 H, OCH$_2$ isomer B), 4.23 (s, 1.33 H, SCH$_2$ isomer A), 7.15-7.35 (m, 1 H, ArH), 7.48 (t, $J=7.6$ Hz, 1.33 H, ArH isomer A), 7.58 (t, $J=7.2$ Hz, 0.66 H, ArH isomer B), 7.89 (t, $J=8$ Hz, 0.66 H, ArH isomer B), 7.99 (t, $J=7.6$ Hz, 1.33 H, ArH isomer A).

**13C-NMR** (CDCl$_3$) $\delta$ 14.6 (CH$_3$ isomer A), 14.8 (CH$_3$ isomer B), 37.3 (SCH$_2$ isomer A), 37.5 (SCH$_3$ isomer B), 51.8 (OCH$_3$ isomer B), 51.9 (OCH$_3$ isomer A), 69.8 (OCH$_2$ isomer A), 70.0 (OCH$_2$ isomer B), 119.0 (C= isomer A), 120.6 (C= isomer B), 128.42, 128.44, 128.65, 128.68, 130.0 and 130.1 (CH Ar), 133.4 and 133.5 (C Ar), 160.9, 163.5, 165.9 and 168.2 (CO ester and C=), 193.5 and 193.9 (CO ketone).

**MS** (Cl) $m/z$ 357 (MH$^+$), 374 (MNH$_4^+$).

![Diethyl 2-oxo-4-phenylthiophene-3,3-dicarboxylate 15](Image)

To a solution of ketene acetal 3c (40 mg, 0.11 mmol) in CH$_2$Cl$_2$ (0.11 mL) was added triflic acid (48 $\mu$L, 0.55 mmol) and stirred at room temperature for 3 h and then heated at reflux temperature for another 3 h. After that time, the reaction mixture was diluted with CH$_2$Cl$_2$ and washed with aqueous saturated NaHCO$_3$ solution. The organic layer was dried and evaporated. The residue was purified by flash column chromatography (petrol:EtOAc 9:1) and the desired heterocycle was obtained as a yellow oil (18 mg, 51%).
The title compound was synthesised by reaction of freshly prepared phenylmagnesium bromide with CS$_2$ and diethyl bromomalonate in THF.

Red oil, petrol:EtOAc 98:2.  
IR (CCl$_4$) $\nu_{\text{max}}$ cm$^{-1}$ 1743 (CO, CS).  
$^1$H-NMR (CDCl$_3$) $\delta$ 1.37 (t, $J$ = 7.2 Hz, 6 H, 2 CH$_3$), 1.35 (q, $J$ = 7.2 Hz, 4 H, 2 OCH$_2$), 5.70 (s, 1 H, CHS), 7.46 (t, $J$ = 8 Hz, 2 H, ArH), 7.62 (t, $J$ = 7.2 Hz, 1 H, ArH), 8.08 (dd, $J$ = 1.2, 8.4 Hz, 2 H, ArH).  
$^{13}$C-NMR (CDCl$_3$) $\delta$ 114.1 (CH), 173.2 (CO).  
HRMS calculated for C$_{16}$H$_{16}$O$_2$S 323.0706 found 323.0712.

Diethyl 2-thiobenzoylsulfanylmalonate 16

Yellow oil, petrol:EtOAc 9:1, method A.  
IR (CCl$_4$) $\nu_{\text{max}}$ cm$^{-1}$ 1718 (CO), 1557 (C=C).  
$^1$H-NMR (CDCl$_3$) $\delta$ 0.94 (t, $J$ = 7 Hz, 3 H, CH$_3$), 1.37 (t, $J$ = 7.2 Hz, 3 H, CH$_3$), 1.85 (s, 3 H, SCH$_3$), 3.92 (q, $J$ = 7.2 Hz, 2 H, OCH$_2$), 4.35 (q, $J$ = 7.2 Hz, 2 H, OCH$_2$), 7.19-7.50 (m, 5 H, ArH).  
$^{13}$C-NMR (CDCl$_3$) $\delta$ 13.6 (CH$_3$), 14.2 (CH$_3$), 16.2 (SCH$_3$), 61.0 (OCH$_2$), 61.1 (OCH$_2$), 128.1, 128.4 and 128.8 (CH Ar), 135.5 (C Ar), 162.7, 164.0 and 165.3 (2 CO and C=).  
MS (Cl) m/z 319 (MH$^+$), 330 (MNH$_4^+$).  
HRMS calculated for C$_{14}$H$_{15}$O$_2$S$_2$ 312.0490 found 312.0492.

Diethyl 2-(1-methylsulfanyl-1-phenylmethylene)malonate 17

Red oil, petrol:EtOAc 95:5.  
IR (CCl$_4$) $\nu_{\text{max}}$ cm$^{-1}$ 1734 (CO).  
$^1$H-NMR (CDCl$_3$) $\delta$ 1.33 (t, $J$ = 7.2 Hz, 6 H, 2 CH$_3$), 4.25-4.40 (m, 4 H, 2 OCH$_2$), 2.17 (s, 3 H, SCH$_3$), 7.43 (t, $J$ = 6.8 Hz, 2 H, ArH), 7.59 (t, $J$ = 7.4 Hz, 1 H, ArH), 8.00 (dd, $J$ = 1.6, 8 Hz, 2 H, ArH).  
$^{13}$C-NMR (CDCl$_3$) $\delta$ 14.0 (2 CH$_3$), 20.7 (SCH$_3$), 63.0 (2 OCH$_2$), 64.7 (C), 126.7, 128.4 and 132.7 (CH Ar), 144.8 (C Ar), 167.5 (2 CO), 224.8 (C=S).  
MS (Cl) m/z 327 (MH$^+$), 344 (MNH$_4^+$).  
HRMS calculated for C$_{15}$H$_{17}$O$_2$S$_2$ 326.0647 found 326.0647.