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# Reaction Between Triphenylphosphine and Acetylenic Esters or Acetylenic Ketones in the Presence of Mercaptoesters

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# Reaction Between Triphenylphosphine and Acetylenic Esters or Acetylenic Ketones in the Presence of Mercaptoesters

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**Abstract:** The reactive diionic intermediate generated by the addition of triphenylphosphine to electron-deficient acetylenic esters or ketones was trapped by mercaptoesters such as mercaptothioglycolate or methyl 3-mercaptopropanoate to produce substituted furans, vinyl sulfides, or dithioesters.

**Keywords:** Acetylenic esters, acetylenic ketones, mercaptoesters, substituted furans, triphenylphosphine

The nucleophilic addition of triphenylphosphine to electron-deficient triple bonds leads to a highly reactive zwitterionic intermediate, which may be trapped by various electrophiles. The reaction of triphenylphosphine with dimethyl acetylenedicarboxylate (DMAD) in the presence of different organic acidic compounds, to trap the diionic intermediate, has been extensively investigated.[1–3] In the most of these reactions, the phosphorus ylides were reported as intermediate or final product. However, there are also many reports on the reaction between triphenylphosphine and acetylenic esters in the presence of an electrophile in which triphenylphosphine acted as catalyst.[4–7] In fact, in these reactions, nucleophilic triphenylphosphine connected together the two electrophilic

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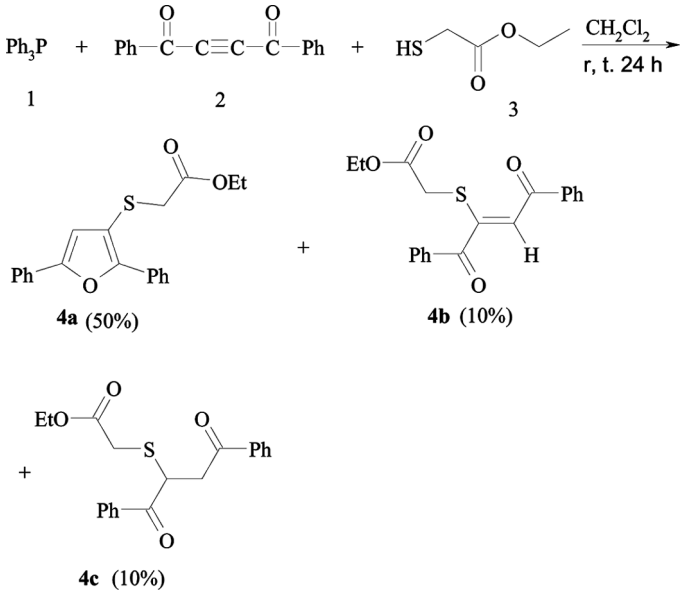
substrates. In continuation of our previous work on the reaction between trivalent phosphorus nucleophiles with acetylenic esters in the presence of organic acidic compounds,[8–11] here we report the results of our studies on the reaction between triphenylphosphine and electron-deficient acetylenic ketones or esters in the presence of S-H acidic compounds such as mercaptothioglycolate or methyl 3-mercaptopropanoate.

Treatment of triphenylphosphine (**1**), dibenzoylacetylene (**2**), and ethyl thioglycolate (**3**) in dichloromethane (DCM) at room temperature for 24 h and separation of the reaction mixture by column chromatography afforded three products: ethyl (2,5-diphenyl-furan-3-ylsulfanyl) acetate **4a** (50% yield), ethyl (1-benzoyl-3-oxo-3-phenyl-propenylsulfanyl) acetate **4b** (10% yield), and ethyl (1-benzoyl-3-oxo-3-phenyl-propyl-sulfanyl)acetate **4c** (10% yield) (Scheme 1).

The structure of products was elucidated from their elemental analysis, $^{1}$H NMR, $^{13}$C NMR, infrared (IR) spectroscopic, and mass spectral data. The $^{1}$H NMR spectrum of compound **4a** exhibited two singlets at δ 3.51 and 6.95 ppm for methylene protons and the proton of furan ring, respectively. A triplet (δ = 1.24 ppm) and a quartet (δ = 4.21 ppm) were observed for ethyl protons. Aromatic protons appeared as multiplets at δ = 7.34–8.22 ppm. $^{13}$C NMR spectrum of compound **4a** exhibited 16




***Scheme 1.*** Reaction of dibenzoylacetylene, triphenylphosphine, and ethyl thioglycolate.

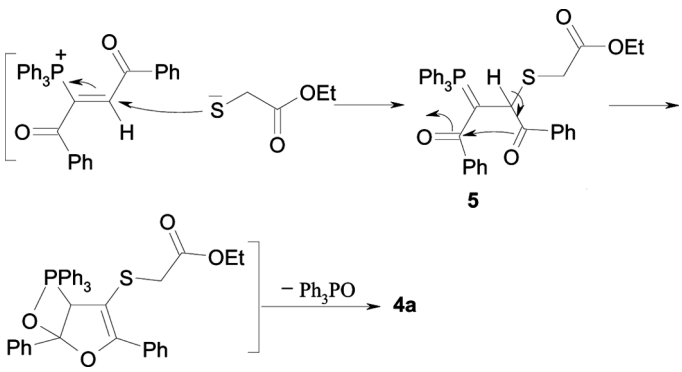
distinct signals, in agreement with the proposed structure. No signal was observed at more than 169 ppm, indicating the absence of a ketone group. The IR spectrum of compound **4a** showed the carbonyl group absorption bond at 1735 $cm^{-1}$. The mass spectrum of compound **4a** showed a molecular ion peak at 338.

For compound **4b**, the chemical shift for the olefinic proton can be used to determine the geometry of double bond.[12] The chemical shift of 7.23 ppm of the olefinic proton is consistent with the *Z*-geometry of the carbon–carbon double bond in compound **4b**.

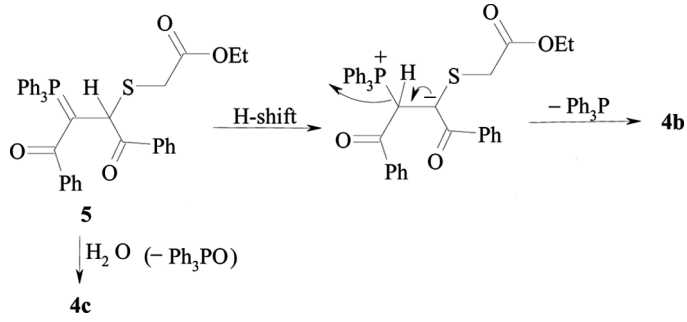
$^1$H NMR spectrum of compound **4c** showed three doublets of doublets at δ 3.52, 4.04, and 5.01 ppm for methylene and methine protons, forming an AMX spinning system. The diastereotopic protons of methylene group attached to sulfur atom resonated at δ = 3.30 ppm as an AB quartet.

On the basis of the well-established chemistry of trivalent phosphorus compounds,[3,7–9] it is reasonable to assume that compound **4a** was obtained from the initial addition of triphenylphosphine to dibenzoylacetylene and subsequent protonation of the reactive diionic adduct by ethyl thioglycolate, followed by the attack of thiolate anion to phosphonium cation to furnish ylide **5**. Rearrangement of ylide **5** followed by elimination of triphenylphosphinoxide resulted in compound **4a** (Scheme 2). Phosphorane **5** may be hydrolized to sulfide **4c** or converted to vinylsulfide **4b** by elimination of triphenylphosphine (Scheme 3).

From the reaction of triphenylphosphine, dibenzoylacetylene, and methyl 3-mercaptopropanoate, sulfur-substituted furan **7a** and isomeric mixtures of vinyl sulfide **7b** were obtained in 65% and 23% yields, respectively (Scheme 4). The chemical shift for the olefinic proton of compound **7b** was used to determine the geometry of the double bond.[12] The




***Scheme 2.*** Suggested mechanism for formation of compound **4a.**

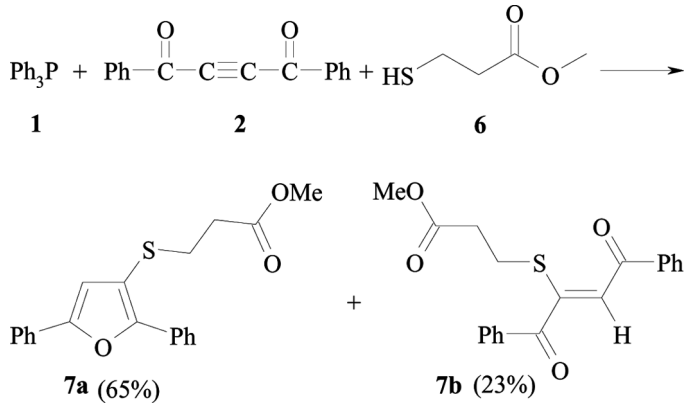



*Scheme 3.* Suggested mechanism for formation of compounds **4b** and **4d**.

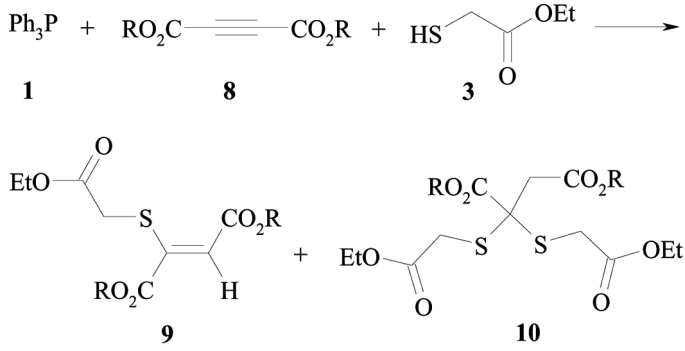


$^1$H NMR, $^{13}$C NMR, and IR spectra of compounds **7a** and **7b** exhibited the characteristic signals and absorption bonds similar to compounds **4a** and **4b**, respectively (see the Experimental Section).

In similar conditions, the reaction of dialkyl acetylenedicarboxylates and triphenylphosphine in the presence of ethyl thioglycolate was studied. Treatment of triphenylphosphine (**1**), dimethyl acetylenedicarboxylate (DMAD, **8a**), and ethyl thioglycolate (**3**) in DCM at room temperature for 24 h and separation of the reaction mixture by column chromatography led to two products: dimethyl 2-(ethoxycarbonyl-methyl sulfanyl)-2-butenoate (**9a**) and dimethyl 2,2-bis-(ethoxycarbonyl-methyl sulfanyl)succinate (**10a**) in 65 and 15% yield, respectively (Scheme 5). Two ethoxycarbonyl-methyl sulfanyl groups are enantiotopic, and four signals for their carbons were obsereved in the $^{13}$C NMR spectrum of




*Scheme 4.* Reaction of dibenzoylacetylene, triphenylphosphine, and methyl 3-mercaptopropanoate.




| 8, 9, 10 | R | Yield% of **9** | Yield% of **10** |
|---|---|---|---|
| **a** | Me | 65 | 15 |
| **b** | Et | 73 | 12 |
| **c** | t-Bu | 68 | 10 |

***Scheme 5.*** Reaction of dialkyl acetylenedicarboxylate, triphenylphosphine, and ethyl thioglycolate.



compound **10a**, so 10 signals were observed in $^{13}C$ NMR spectrum of compound **10a**, in agreement with the proposed structure. However, the protons of methylene groups connected to sulfur atoms are diastereotopic, and a multiplet was observed for them in the $^{1}H$ NMR spectrum of compound **10a**. The protons of the methylene group connected to quaternary carbon atom are enantiotopic, and a single signal was observed for them at $\delta = 3.81$ ppm.

A reasonable mechanism for formation of compound **9a** is similar to that explained for compound **4a** (Scheme 2). Compound **10** was probably formed from the Michael addition of another molecule of ethyl thioglycolate to vinylsulfide **9**. When the reaction was carried out with 2 equivalents of ethyl thioglycolate, compound **10a** was obtained in 95% yield as the only product. As shown in Scheme 5, the reaction was applicable for other acetylene diesters, such as diethyl or ditertiobutyl acetylenedicarboxylate, and products **9b** and **c** and **10b** and **c** were obtained.

Under similar conditions, the reaction of thiophenol was examined with acetylenic esters or ketones in the presence of triphenylphosphine, but no product was obtained.

In conclusion, the reaction of dibenzoylacetylene, triphenylphosphine, and ethylthioglycolate or methyl 3-mercaptopropanoate furnished a simple one-pot route to sulfur-substituted furans as main product. A similar reaction with dialkyl acetylendicarboxylates, instead of dibenzoylacetylene, resulted in vinylsulfides in moderate yields and

dithioacetals as minor product. In this method, not only was the reaction performed under neutral conditions but also the starting materials and reagents can be mixed without any activation or modification.

## EXPERIMENTAL

Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a Finnigan-Mat 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. $^{1}H$ and $^{13}C$ NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500 and 125.8 MHz, respectively. $^{1}H$ and $^{13}C$ spectra were obtained on solution in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Dibenzoylacetylene was prepared by addition of acetylenedimagnesium-dibromide[10] to benzaldehyde and oxidation of the obtained diol.[11] Other chemicals used in this work were purchased from Fluka (Buchs, Switzerland).



### General Procedure

A mixture of acetylenic compound (2 mmol) in 5 ml DCM was added to a magnetically stirred solution of mercaptoester (2 mmol) and triphenylphosphine (2 mmol) in 10 ml DCM at room temperature over 10 min. The reaction mixture was then allowed to stir for 24 h. The solvent was removed under reduced pressure, and the residue was purified by silica-gel (Merck silica gel 60, 230–400 mesh) column chromatography using hexane–ethyl acetate as eluent.

### Data

Ethyl (2,5-Diphenyl-furan-3-yl-sulfanyl) Acetate (**4a**)

Yellow oil; yield 0.34 g (50%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1735 (C=O). MS, $m/z$ (%): 338 ($M^+$, 75), 223 (74), 105 (COPh, 83), 77 (Ph, 100). Anal. calcd. for $C_{20}H_{18}O_3S$ (338.4): C, 70.98; H, 5.36. Found: C, 70.9; H, 5.5%. $^{1}H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.24$ (3 H, t $^{3}J_{HH}$ 7 Hz, $CH_3$), 3.51 (2 H, s, $SCH_2$), 4.21 (2 H, q $^{3}J_{HH}$ 7 Hz, $OCH_2$), 6.95 (1 H, s, olefinic CH), 7.34–8.22 (10 H, m, 2 $C_6H_5$). $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 13.8$ ($CH_3$), 37.4 ($SCH_2$), 61.3 ($OCH_2$), 111.4, 113.0, 151.8, and

152.3 (furan moiety), 123.7, 125.7, 127.7, 127.7, 128.3, 128.7, 129.8, and 130.1 (2 $C_6H_5$), 169.3 (CO).

Ethyl (1-Benzoyl-3-oxo-3-phenyl-propenylsulfanyl) Acetate (**4b**)

Yellow oil; yield 0.07 g (10%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1744 (C=O, ester), 1668, and 1641 (2 C=O, ketone). MS, $m/z$ (%): 354 ($M^+$, 89), 267 (74), 235 (81), 105 (COPh, 100), 77 (Ph, 99). Anal. calcd. for $C_{20}H_{18}O_4S$ (354.4): C, 67.78; H, 5.12. Found: C, 67.6; H, 5.1%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.31$ (3 H, t $^3J_{HH}$ 7 Hz, $CH_3$), 3.64 (2 H, s, $SCH_2$), 4.23 (2 H, q $^3J_{HH}$ 7 Hz, $OCH_2$), 7.23 (1 H, s, CH), 7.32–8.20 (10 H, m, 2 $C_6H_5$). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 13.8$ ($CH_3$), 33.9 ($SCH_2$), 62.2 ($OCH_2$), 117.7 and 156.7 (olefinic carbons), 128.4, 128.6, 129.6, 129.7, 132.9, 133.6, 134.5, and 136.8 (2 $C_6H_5$), 167.6 (CO ester), 185.1 and 193.0 (2 CO ketone).

Ethyl (1-Benzoyl-3-oxo-3-phenyl-propylsulfanyl) Acetate (**4c**)

Yellow oil; yield 0.07 g (10%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1730 (C=O, ester), 1676 (C=O, ketone). MS, $m/z$ (%): 356 ($M^+$, 2), 223 (24), 105 (COPh, 100), 77 (Ph, 99). Anal. calcd. for $C_{20}H_{20}O_4S$ (356.4): C, 67.39; H, 5.66. Found: C, 67.3; H, 5.7%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.31$ (3 H, t $^3J_{HH}$ 7 Hz, $CH_3$), 3.30 (2 H, AB-quartet, $SCH_2$), 3.52 (1 H, dd $^2J_{HH}$ 18 Hz, $^3J_{HH}$ 4 Hz, *H*CH), 4.04 (1 H, dd $^2J_{HH}$ 18 Hz, $^3J_{HH}$ 10 Hz, *H*CH), 4.22 (2 H, q $^3J_{HH}$ 7 Hz, $OCH_2$), 5.01 (1 H, dd $^3J_{HH}$ 4 Hz, $^3J_{HH}$ 10 Hz, CH), 7.41–7.75 (6 H, m, 6CH), 7.91 (2 H, d $^3J_{HH}$ 8 Hz, 2 $CH_{ortho}$), 8.13 (2 H, d $^3J_{HH}$ 8 Hz, 2 $CH_{ortho}$). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 14.0$ ($CH_3$), 31.8 ($SCH_2$), 41.3 and 41.4 (CH and $CH_2$), 61.7 ($OCH_2$), 128.1, 128.6, 128.7, 128.8, 133.3, 133.5, 135.6 and 136.0 (2 $C_6H_5$), 163.9, 188.9, and 191.3 (3 CO).

Methyl 3-(2,5-Diphenyl Furan-3-ylsulfanyl) Propanoate (**7a**)

Yellow oil; yield 0.44 g (65%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1735 (C=O). MS, $m/z$ (%): 338 ($M^+$, 77), 223 (63), 105 (COPh, 55), 77 (Ph, 100). Anal. calcd. for $C_{20}H_{18}O_3S$ (338.4): C, 70.98; H, 5.36. Found: C, 70.9; H, 5.2%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.62$ and 3.13 (4 H, 2 t $^3J_{HH}$ 7 Hz, 2 $CH_2$), 3.72 (3 H, s, $CH_3$), 6.80 (1 H, s, CH), 7.29–8.18 (10 H, m, 2 $C_6H_5$). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 30.4$ and 33.1 (2 $CH_2$), 51.7 ($CH_3$), 111.5, 113.5, 151.9 and 152.5 (furan moiety), 123.8, 125.8, 127.8, 127.9, 128.4, 128.9, 130.4, 130.5 (2 $C_6H_5$), 169.3 (CO).

Methyl 3-(1-Benzoyl-3-oxo-3-phenylpropenylsulfanyl) Propanoate (**7b**)

Yellow oil; yield 0.16 g (23%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1731 (C=O, ester), 1665, and 1633 (2 C=O, ketone). MS, $m/z$ (%): 354 ($M^+$, 81), 267 (84), 235 (90), 105 (COPh, 100), 77 (Ph, 99). Anal. calcd. for $C_{20}H_{18}O_4S$ (354.4): C, 67.78; H, 5.12. Found: C, 67.6; H, 5.1%. NMR data for $Z$ isomer (65%): $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 2.49$ and 2.81 (4 H, 2 t $^3J_{HH}$ 8 Hz, 2 $CH_2$), 3.57 (3 H, s, $CH_3$), 7.11 (1 H, s, olefinic proton), 7.31–8.16 (10 H, m, 2 $C_6H_5$). $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 27.0$ and 33.9 (2 $CH_2$), 51.9 ($CH_3$), 117.0 and 158.7 (olefinic carbons), 128.1, 128.7, 129.1, 130.1, 132.8, 134.2, 133.7, and 137.7 (2 $C_6H_5$), 171.3, 188.2, and 191.8 (3 CO); NMR data for $E$ isomer (25%): $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 2.69$ and 3.15 (4 H, 2 t $^3J_{HH}$ 8 Hz, 2 $CH_2$), 3.73 (3 H, s, $CH_3$), 6.89 (1 H, s, olefinic proton), 7.27–8.26 (10 H, m, 2 $C_6H_5$). $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 26.7$ and 33.4 (2 $CH_2$), 52.1 ($CH_3$), 117.5 and 158.1 (olefinic carbons), 128.1, 1285, 128.7, 128.8, 133.2, and 134.8, 133.5, and 137.0 (2 $C_6H_5$), 171.4, 185.3, and 193.3 (3 CO).

Dimethyl 2-Ethoxycarbonylmethylsulfanyl-2-butenoate (**9a**)

Yellow oil; yield 0.16 g (65%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1720 (broad, 3C=O ester), 1583 (C=C). MS, $m/z$ (%): 263 ($M^+ + 1$, 81), 231 ($M^+ - OCH_3$, 100), 216 (231-$CH_3$, 30), 189 ($M^+ - CO_2Et$, 50). Anal. calcd. for $C_{10}H_{14}O_6S$ (262.3): C, 45.79; H, 5.38. Found: C, 45.6; H, 5.3%. NMR data for $Z$ isomer (60%): $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.29$ (3 H, t $^3J_{HH}$ 7 Hz, $CH_3$), 3.70 (2 H, s, $CH_2$), 3.65 and 3.79 (6 H, 2 s, 2 $OCH_3$), 4.32 (2 H, q $^3J_{HH}$ 7 Hz, $OCH_2$), 6.97 (1 H, s, CH); $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 12.1$ ($CH_3$), 34.2 ($CH_2$), 52.1 and 52.2 (2 $OCH_3$), 62.4 ($OCH_2$), 122.3 (CH), 147.2 (C), 168.2, 169.3, and 171.8 (3 CO); NMR data for $E$ isomer (40%): $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.39$ (3 H, t $^3J_{HH}$ 7 Hz, $CH_3$), 3.64 (2 H, s, $CH_2$), 3.67 and 4.15 (6 H, 2 s, 2 $OCH_3$), 4.21 (2 H, q $^3J_{HH}$ 7 Hz, $OCH_2$), 6.21 (1 H, s, CH); $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 12.3$ ($CH_3$), 34.0 ($CH_2$), 51.7 and 52.4 (2 $OCH_3$), 62.1 ($OCH_2$), 122.7 (CH), 146.2 (C), 168.0, 169.0, and 172.3 (3 CO).

Diethyl 2-Ethoxycarbonylmethylsulfanyl-2-butenoate (**9b**)

Yellow oil; yield 0.42 g (73%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1733 (broad, 3 C=O ester), 1583 (C=C). MS, $m/z$ (%): 291 ($M^+ + 1$, 20), 245 ($M^+ - OEt$, 100), 216 (245-Et, 25). Anal. calcd. for $C_{12}H_{18}O_6S$ (290.3): C, 49.64; H, 6.25. Found: C, 49.6; H, 6.3%. NMR data for $Z$ isomer (65%): $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.21$–1.78 (9 H, m, 3 $CH_3$), 3.88 (2 H, s,

$SCH_2$), 4.15–4.71 (6 H, m, 3 $OCH_2$), 6.89 (1 H, s, CH); $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 13.5$, 13.5, and 14.0 (3 $CH_3$), 35.0 ($SCH_2$), 60.9, 61.4, and 62.5 (3 $OCH_2$), 122.3 (CH), 147.8 (C), 165.3, 166.2, and 170.9 (3 CO); NMR data for E isomer (25%): $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.21$–1.78 (9 H, m, 3 $CH_3$), 3.71 (2 H, s, $SCH_2$), 4.15–4.71 (6 H, m, 3 $OCH_2$), 6.01 (1 H, s, CH); $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 13.6$, 13.7, and 13.8 (3 $CH_3$), 33.2 ($SCH_2$), 60.1, 61.8, and 62.4 (3 $OCH_2$), 114.3 (CH), 148.8 (C), 163.3, 165.3, and 168.3 (3 CO).

Di-*tert*-butyl 2-Ethoxycarbonylmethylsulfanyl-2-butenoate (**9c**)

Yellow oil; yield 0.16 g (68%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1737 (broad, 3C=O ester), 1530 (C=C). MS, $m/z$ (%): 346 ($M^+ + 1$, 3), 290 ($M^+ - C_4H_8$, 5), 234 (20), 57 ($C_4H_9$, 100). Anal. calcd. for $C_{16}H_{26}O_6S$ (346.4): C, 55.47; H, 7.56. Found: C, 55.5; H, 7.4%. NMR data for *Z* isomer (55): $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.07$–1.80 (21 H, m, 7 $CH_3$), 3.84 (2 H, s, $SCH_2$), 4.11 (2 H, q, $^3J_{HH}$ 7 Hz, $OCH_2$), 6.75 (1 H, s, CH); $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 13.2$ ($CH_3$), 28.0 and 28.1 (6 $CH_3$), 33.8 ($SCH_2$), 62.1 ($OCH_2$), 82.3 and 84.1 (2 OC), 123.1 (CH), 148.2 (C), 163.1, 165.2, and 170.8 (3 CO); NMR data for *E* isomer (45): $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 1.07$–1.80 (21 H, m, 7 $CH_3$), 3.63 (2 H, s, $SCH_2$), 4.35 (2 H, q, $^3J_{HH}$ 7 Hz, $OCH_2$), 5.78 (1 H, s, CH); $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 13.3$ ($CH_3$), 28.2 (3 $CH_3$), 28.3 (3 $CH_3$), 34.1 ($SCH_2$), 62.4 ($OCH_2$), 81.7 and 83.1 (2 OC), 119.8 (CH), 147.70 (C), 162.8, 164.5, and 170.1 (3 CO).

Dimethyl 2,3-Bis-ethoxycarbonylmethylsulfanylsuccinate (**10a**)

Yellow oil; yield 15%. IR (KBr) ($\nu_{max}/cm^{-1}$): 1723 (C=O). Anal. calcd. for $C_{14}H_{23}O_8S_2$(382.45): C, 43.97; H, 5.80. Found: C, 43.8; H, 5.7%. MS (m/z, %): 383 (M + 1, 66), 266 (100), 231 (99), 145 (79). $^1H$ NMR (500 $MH_Z$, $CDCl_3$): $\delta = 1.32$ (6 H, t $^3J_{HH} = 7\,H_Z$, 2 $CH_3$), 3.36–3.53 (4 H, m, 2 $SCH_2$), 3.71 and 3.79 (6 H, 2 s, 2 $OCH_3$), 3.81 (2 H, s, $CH_2$), 4.25 (4 H, q $^3J_{HH} = 7$ $H_Z$, 2 $OCH_2$).$^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 14.1$ (2 $CH_3$), 33.3 (2 $SCH_2$), 47.0 ($CH_2$), 47.3 (C), 52.7 and 52.8 (2 $OCH_3$), 61.7 (2 $OCH_2$), 169.3, 169.4, and 169.8 (4 C=O).

Diethyl 2,3-Bis-ethoxycarbonylmethylsulfanylsuccinate (**10b**)

Yellow oil; yield 0.10 g (12%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1726 (C=O), MS, $m/z$ (%): 411 ($M^+ + 1$, 15), 337 ($M^+ - CO_2Et$, 11), 291 ($M^+$-$SCH_2CO_2Et$,

77), 245 (291-OEt, 100). Anal. calcd. for $C_{16}H_{26}O_8S_2$ (410.50): C, 46.81; H, 6.38. Found: C, 46.8; H, 6.3%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.21$–1.84 (12 H, 4 $CH_3$), 3.54 (4 H, AB-quartet, 2 $SCH_2$), 3.79 (2 H, s, $CH_2$), 4.10–4.67 (8 H, m, 4 $OCH_2$). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 13.6$ and 14.0, 14.1 (4 $CH_3$), 32.2 (2 $SCH_2$), 47.1 ($CH_2$), 47.5 (C), 61.4, 61.6, and 61.7 (4 $OCH_2$), 169.30, 170.3, and 170.5 (4 CO).

Di-*tert*-butyl 2,3-Bis-ethoxycarbonylmethylsulfanylsuccinate (**10c**)

Yellow oil; yield 0.09 g (10%). IR (KBr) ($\nu_{max}/cm^{-1}$): 1730 (C=O), MS, $m/z$ (%): 466 ($M^+$, 4), 411 ($M^+ - C_4H_7$, 20), 57 ($C_4H_9$, 100). Anal. calcd. for $C_{20}H_{34}O_8S_2$ (466.6): C, 51.48; H, 7.34. Found: C, 51.7; H, 7.3%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.18$–1.80 (24 H, 8 $CH_3$), 3.4 (2 H, s, $CH_2$), 3.75 (4 H, AB-quartet, 2 $SCH_2$), 4.33 (2 H, q, $^3J_{HH}$ 7 Hz, $OCH_2$). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 13.1$ ($CH_3$), 29.0 and 29.0 (6 $CH_3$), 33.0 ($SCH_2$), 47.9 (C), 48.2 ($CH_2$), 62.1 ($OCH_2$), 83.2 and 82.4 (2 OC), 169.7, 170.2, and 170.6 (4 CO).



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