# Diastereoselective Dealkoxycarbonylation of Sulfur-Substituted Dialkyl Cyclopropane-1,1-dicarboxylates

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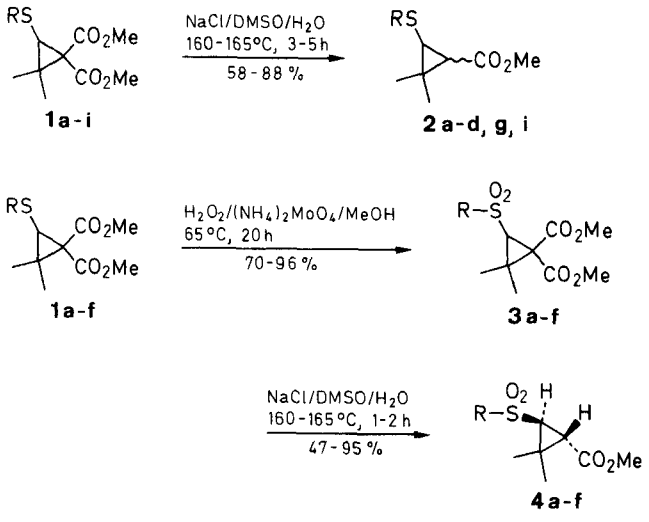
In the dealkoxycarbonylation of dimethyl 2,2-dimethylcyclopropane-1,1-dicarboxylate, 3-alkylthio or 3-arylthio substituents induce moderate diastereoselection. The analogous dealkoxycarbonylation of 3-alkylsulfonyl- or 3-arylsulfonyl-substituted cyclopropanes leads to an *E* diastereoselectivity of 100%.

Electrophilic cyclopropanes have gained increasing importance in organic synthesis being very useful and versatile three carbon building blocks.[1,2] Little is known about the dealkoxycarbonylation of electrophilic cyclopropanes and the results[3-6] are sometimes uncertain and/or peculiar from the mechanistic point of view.[7] It appears that if the cyclopropanes do not possess appropriate steric hindrance, ring-cleavage products are formed instead of those expected from dealkoxycarbonylation. Moreover, no systematic study on stereoselection in the dealkoxycarbonylation of cyclopropanecarboxylic esters has been published.

In continuation of our studies[8] on the stereochemistry of dealkoxycarbonylation, we now report the results obtained with some alkylthio- and arylthiocyclopropane-1,1-dicarboxylic esters of the formula **1a–d,g,i** and with the alkylsulfonyl- and arylsulfonylcyclopropane-1,1-dicarboxylic esters **3a–f**.




| 1 | 2 | 3 | 4 | R |
|---|---|---|---|---|
| a | a | a | a | Et |
| b | b | b | b | $PhCH_2$ |
| c | c | c | c | $HOCH_2CH_2$ |
| d | d | d | d | Ph |
| e | | e | e | $2\text{-}MeC_6H_4$ |
| f | | f | f | $4\text{-}MeC_6H_4$ |
| g | g | | | $2\text{-}MeOC_6H_4$ |
| h | | | | $2\text{-}HO_2CC_6H_4$ |
| i | i | | | $2\text{-}MeO_2CC_6H_4$ |

The cyclopropane-1,1-dicarboxylic esters **1** were chosen because of their easy accessibility and because they were expected to be fairly stable under the conditions of the dealkoxycarbonylation, due to the presence of the geminal methyl groups. Compounds **1** were prepared in 70–95% yields according to the method[9] reported for **1d** by reaction of alkane- or arenethiolates in methanol with dimethyl 2-bromo-2-methylpropylidenemalonate. The sulfones **3a–d** were prepared by oxidation of sulfides **1a–d** with 35% hydrogen peroxide and ammonium molybdate in boiling methanol. Sulfides **1e,f** were oxidized to sulfones **3e,f** with peracetic acid (35% $H_2O_2$ + AcOH) in boiling excess acetic acid. The dealkoxycarbonylations were carried out with sodium chloride (1 equiv) in boiling (160–165°C) dimethyl sulfoxide/water (25:1.8), until development of $CO_2$ ceased.

The dealkoxycarbonylation of the alkylthio or arylthio compounds **1a–d,g,i** in all cases yields esters **2** as a mixture of isomers with the *trans* isomer being in large excess, whereas the dealkoxycarbonylation of the sulfonyl derivatives **3a–f** is diastereoselective leading exclusively to the cyclopropane *trans*-derivatives **4** in good yields.

From these results it can be concluded that:

(1) The presence of the sulfenyl or the sulfonyl groups appears to be necessary for the reaction to be diastereoselective in view of the fact that, e.g., the demethoxycarbonylation of dimethyl 3-cyano-2,2-dimethylcyclopropane-1,1-dicarboxylate under the same conditions (DMSO/$H_2O$/NaCl) leads to a *trans*/*cis* ratio of 53:47.[10]

(2) The stereochemical outcome should be determined by the protonation of an intermediate ester enolate and could be the result of thermodynamic control, providing the more stable *trans* isomers. Nevertheless, the two methoxycarbonyl groups might also react at different rates due to steric hindrance[11] by the sulfenyl or sulfonyl groups, as evidenced by the fact that upon treatment of **1d** with methanolic potassium hydroxide at reflux temperature for 6 h, only the 1,1-dicarboxylic acid *cis*-monoester **5** was obtained[13] by hydrolysis of the *trans*-methoxycarbonyl group.

(3) The higher trans/cis ratio of in the case **2c** might be due to the relatively high acidity of the hydroxy group which could act as an intramolecular proton donor.

**Table 1.** Dimethyl Cyclopropane-1,1-dicarboxylates **1**[a] Prepared

| Product | Yield[b] (%) | bp (°C)/Torr or mp (°C) (solvent) | Molecular Formula[c] | $^1$H-NMR ($CDCl_3$/TMS) $\delta$, $J$(Hz) |
|---|---|---|---|---|
| **1c** | 70 | 140/1 | $C_{11}H_{18}O_5S$ (263.25) | 1.22 (s, 3H, $CH_3$), 1.30 (s, 3H, $CH_3$), 2.70 (s, 1H, CH), 2.76 (t, 2H, $J$ = 5.7, $SCH_2$), 2.93 (s, 1H, OH), 3.70 (s, 3H, $CO_2CH_3$), 3.70 (t, 2H, $J$ = 5.7, $OCH_2$), 3.73 (s, 3H, $CO_2CH_3$) |
| **1e** | 98 | 34[d] | $C_{16}H_{20}O_4S$ (308.3) | 1.33 (s, 6H, $CH_3$), 2.24 (s, 3H, $CH_3$), 3.06 (s, 1H, CH), 3.60 (s, 3H, $CO_2CH_3$), 3.70 (s, 3H, $CO_2CH_3$), 7.10 (m, 4H$_{arom}$) |
| **1f** | 91 | 70 (MeOH) | $C_{16}H_{20}O_4S$ (308.3) | 1.23 (s, 3H, $CH_3$), 1.28 (s, 3H, $CH_3$), 2.20 (s, 3H, $CH_3$), 3.07 (s, 1H, CH), 3.62 (s, 3H, $CO_2CH_3$), 3.69 (s, 3H, $CO_2CH_3$), 7.10 (m, 4H$_{arom}$) |
| **1g** | 80 | [e] | $C_{16}H_{20}O_5S$ (324.3) | 1.26 (s, 3H, $CH_3$), 1.30 (s, 3H, $CH_3$), 3.00 (s, 1H, CH), 3.52 (s, 3H, $OCH_3$), 3.67 (s, 3H, $CO_2CH_3$), 3.73 (s, 3H, $CO_2CH_3$), 7.10 (m, 4H$_{arom}$) |
| **1h** | 69 | 182 (EtOH) | $C_{16}H_{18}O_6S$ (338.3) | 1.38 (s, 3H, $CH_3$), 1.42 (s, 3H, $CH_3$), 3.05 (s, 1H, CH), 3.63 (s, 3H, $CO_2CH_3$), 3.82 (s, 3H, $CO_2CH_3$), 7.60 (m, 4H$_{arom}$), 10.40 (s, 1H, $CO_2H$) |
| **1i** | 65 | [f] | $C_{17}H_{20}O_6S$ (352.3) | 1.35 (s, 3H, $CH_3$), 1.40 (s, 3H, $CH_3$), 3.00 (s, 1H, CH), 3.60 (s, 3H, $CO_2CH_3$), 3.78 (s, 3H, $CO_2CH_3$), 3.88 (s, 3H, $CO_2CH_3$), 7.60 (m, 4H$_{arom}$) |

[a] Products **1a**, **b**, **d** are known compounds.[9]
[b] Yields of isolated product.
[c] Satisfactory microanalyses: C ±0.2, H ±0.09, S ±0.13.
[d] Chromatographed on a silica gel column using $Et_2O$/petroleum ether (bp 40–70 °C) (1:1) as eluent.
[e] Refractive index determined after chromatography as in footnote d: $n_D^{16} = 1.5460$.
[f] Obtained by refluxing 1 h in MeOH for 20 h with a few drops of conc. $H_2SO_4$. The ester is then chromatographed as in footnote d; $n_D^{20} = 1.5435$.

**Table 2.** Methyl Cyclopropanecarboxylates **2** Prepared

| Product | Reaction Time (h) | Yield[a] (%) | $E/Z$[b] Ratio | $n_D$ (°C)[c] | Molecular Formula[d] | Isomer | $^1$H-NMR ($CDCl_3$/TMS)[e] $\delta$, $J$(Hz) |
|---|---|---|---|---|---|---|---|
| **2a** | 5 | 86 | 62:38 | 1.4787 (18) | $C_9H_{16}O_2S$ (188.2) | *cis* | 1.1–1.38 (m, 9H, $3CH_3$), 1.70 (d, 1H, CH, $J$ = 8.6), 2.15 (d, 1H, $J$ = 8.6, CH), 2.50 (q, 2H, $J$ = 7.4, $CH_2CH_3$), 3.61 (s, 3H, $CO_2CH_3$) |
| | | | | | | *trans* | 1.1–1.38 (m, 9H, $3CH_3$), 1.50 (d, 1H, $J$ = 5.1, CH), 2.45 (d, 1H, $J$ = 5.1, CH), 2.55 (q, 2H, $J$ = 7.4, $CH_2CH_3$), 3.62 (s, 3H, $CO_2CH_3$) |
| **2b** | 3 | 88 | 65:35 | 1.5370 (20) | $C_{14}H_{18}O_2S$ (250.3) | *cis* | 1.03 (s, 3H, $CH_3$), 1.10 (s, 3H, $CH_3$), 1.60 (d, 1H, $J$ = 9, CH), 1.93 (d, 1H, $J$ = 9, CH), 3.57 (s, 2H, $CH_2$), 3.64 (s, 3H, $CO_2CH_3$), 7.95 (s, 5H$_{arom}$) |
| | | | | | | *trans* | 1.03 (s, 3H, $CH_3$), 1.10 (s, 3H, $CH_3$), 1.30 (d, 1H, $J$ = 5.0, CH), 2.30 (d, 1H, $J$ = 5.0, CH), 3.52 (s, 3H, $CO_2CH_3$), 3.57 (s, 2H, $CH_2$), 7.95 (s, 5H$_{arom}$) |
| **2c** | 5 | 58 | 79:21 | 1.5018 (18) | $C_9H_{16}O_3S$ (204.2) | *cis* | 1.21 (s, 3H, $CH_3$), 1.32 (s, 3H, $CH_3$), 1.70 (d, 1H, $J$ = 8.0, CH), 2.15 (d, 1H, $J$ = 8.0, CH), 2.65 (t, 2H, $J$ = 6.2, $SCH_2$), 2.95 (s, 1H, OH), 3.65 (s, 3H, $CO_2CH_3$), 3.70 (t, 2H, $J$ = 6.2, $CH_2O$) |
| | | | | | | *trans* | 1.22 (s, 3H, $CH_3$), 1.32 (s, 3H, $CH_3$), 1.50 (d, 1H, $J$ = 5.0, CH), 2.45 (d, 1H, $J$ = 5.0, CH), 2.65 (t, 2H, $J$ = 6.2, $SCH_2$), 2.95 (s, 1H, OH), 3.65 (s, 3H, $CO_2CH_3$), 3.70 (t, 2H, $J$ = 6.2, $CH_2O$) |
| **2d** | 5 | 75 | 67:33 | 1.5490 (20) | $C_{13}H_{16}O_2S$ (236.3) | *cis* | 1.30 (s, 3H, $CH_3$), 1.38 (s, 3H, $CH_3$), 1.81 (d, 1H, $J$ = 9.0, CH), 2.40 (d, 1H, $J$ = 9.0, CH), 3.55 (s, 3H, $CO_2CH_3$), 7.18 (s, 5H$_{arom}$) |
| | | | | | | *trans* | 1.30 (s, 3H, $CH_3$), 1.38 (s, 3H, $CH_3$), 1.60 (d, 1H, $J$ = 5.0, CH), 2.77 (d, 1H, $J$ = 5.0, CH), 3.68 (s, 3H, $CO_2CH_3$), 7.18 (s, 5H$_{arom}$) |
| **2g** | 5 | 79 | 65:35 | 1.5580 (20) | $C_{14}H_{18}O_3S$ (266.3) | *cis* | 1.27 (s, 3H, $CH_3$), 1.29 (s, 3H, $CH_3$), 1.85 (d, 1H, $J$ = 8.8, CH), 2.38 (d, 1H, $J$ = 8.8, CH), 3.54 (s, 3H, $CH_3O$), 3.77 (s, 3H, $CO_2CH_3$), 6.90 (m, 4H$_{arom}$) |
| | | | | | | *trans* | 1.24 (s, 3H, $CH_3$), 1.32 (s, 3H, $CH_3$), 1.61 (d, 1H, $J$ = 5.0, CH), 2.63 (d, 1H, $J$ = 5.0, CH), 3.62 (s, 3H, $CO_2CH_3$), 3.77 (s, 3H, $CO_2CH_3$), 6.90 (m, 4H$_{arom}$) |

**Table 2.** (continued)

| Product | Reaction Time (h) | Yield[a] (%) | $E/Z$[b] Ratio | $n_D$ (°C)[c] | Molecular Formula[d] | Isomer | $^1$H-NMR ($CDCl_3$/TMS)[e] $\delta$, $J$(Hz) |
|---|---|---|---|---|---|---|---|
| **2i** | 5 | 60 | 68 : 32 | 1.5321[f] (18) | $C_{15}H_{18}O_4S$ (294.3) | *cis*[f] | 1.32 (s, 6H, $2CH_3$), 1.98 (d, 1H, $J$ = 8.7, CH), 2.38 (d, 1H, $J$ = 8.7, CH), 3.57 (s, 3H, $CO_2CH_3$), 3.88 (s, 3H, $CO_2CH_3$), 7.47 (m, $4H_{arom}$) |
| | | | | 1.5563[f] (18) | $C_{15}H_{18}O_4S$ (294.3) | *trans*[f] | 1.23 (s, 3H, $CH_3$), 1.37 (s, 3H, $CH_3$), 1.69 (d, 1H, $J$ = 5.1, CH), 2.69 (d, 1H, $J$ = 5.1, CH), 3.65 (s, 3H, $CO_2CH_3$), 3.80 (s, 3H, $CO_2CH_3$), 7.47 (m, $4H_{arom}$) |

[a] Yields of isolated product.
[b] Obtained from the ratio of the $^1$H-NMR integrals of the doublets of the cyclopropyl protons; $E$: $J_{H-H}$ = 5.0–5.1 Hz; $Z$: $J_{H-H}$ = 7.5–9.0 Hz.[15]
[c] Values of the mixture of the two isomers.
[d] Satisfactory microanalyses: C ±0.37, H ±0.28, S ±0.14.
[e] Chemical shifts from the spectra of the mixture of the two isomers.
[f] Single isomers were isolated by chromatography on a silica gel column using $Et_2O$/petroleum ether (bp 40–70°C) (1:1) as eluent.

**Table 3.** Dimethyl Sulfonylcyclopropane-1,1-dicarboxylates[a] **3** Prepared

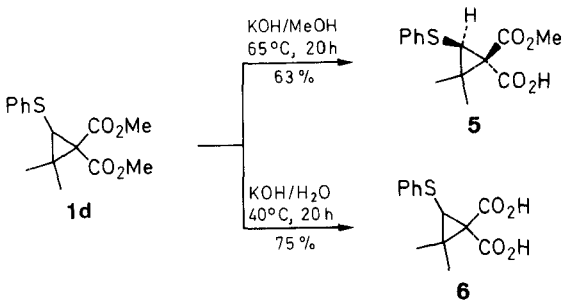
| Product | Yield[b] (%) | mp (°C) (solvent) | Molecular Formula[c] | $^1$H-NMR ($CDCl_3$/TMS) $\delta$, $J$(Hz) |
|---|---|---|---|---|
| **3a** | 90 | 71 (hexane) | $C_{11}H_{18}O_6S$ (278.25) | 1.20 (s, 3H, $CH_3$), 1.35 (t, 3H, $J$ = 7.0, $CH_3$), 1.65 (s, 3H, $CH_3$), 3.03 (s, 1H, CH), 3.12 (q, 2H, $J$ = 7.0, $CH_2$), 3.73 (s, 6H, $CO_2CH_3$) |
| **3b** | 70 | 109 (EtOH) | $C_{16}H_{20}O_6S$ (340.3) | 1.10 (s, 3H, $CH_3$), 1.52 (s, 3H, $CH_3$), 2.90 (s, 1H, CH), 3.73 (s, 3H, $CO_2CH_3$), 3.75 (s, 3H, $CO_2CH_3$), 4.31 (q, 2H, $J$ = 13.9, $CH_2$), 7.35 (s, $5H_{arom}$) |
| **3c** | 83 | 71–72[d] | $C_{11}H_{18}O_7S$ (294.25) | 1.22 (s, 3H, $CH_3$), 1.65 (s, 3H, $CH_3$), 2.79 (s, 1H, OH), 3.23 (s, 1H, CH), 3.31 (t, 2H, $J$ = 6.1, $CH_2OH$), 3.74 (s, 6H, $CO_2CH_3$), 4.01 (t, 2H, $J$ = 6.1, $SO_2CH_2$) |
| **3d** | 96 | 108 (EtOH) | $C_{15}H_{18}O_6S$ (326.3) | 1.13 (s, 3H, $CH_3$), 1.70 (s, 3H, $CH_3$), 3.15 (s, 1H, CH), 3.68 (s, 3H, $CO_2CH_3$), 3.80 (s, 3H, $CO_2CH_3$), 7.70 (m, $5H_{arom}$) |
| **3e** | 95 | oil[e] | $C_{16}H_{20}O_6S$ (340.3) | 1.24 (s, 3H, $CH_3$), 1.61 (s, 3H, $CH_3$), 2.70 (s, 3H, $CH_3$), 3.31 (s, 1H, CH), 3.65 (s, 3H, $CO_2CH_3$), 3.71 (s, 3H, $CO_2CH_3$), 7.75 (m, $4H_{arom}$) |
| **3f** | 85 | 175 (MeOH) | $C_{16}H_{20}O_6S$ (340.3) | 1.14 (s, 3H, $CH_3$), 1.68 (s, 3H, $CH_3$), 2.39 (s, 3H, $CH_3$), 3.13 (s, 1H, CH), 3.66 (s, 3H, $CO_2CH_3$), 3.78 (s, 3H, $CO_2CH_3$), 7.53 (m, $4H_{arom}$) |

[a] The $SO_2$ vibrations (1115–1120, 1310–1320 $cm^{-1}$) are present in all IR spectra (nujol).
[b] Yields of isolated product.
[c] Satisfactory microanalyses: C ±0.28, H ±0.25, S ±0.19.
[d] Chromatographed on a silica gel column using $Et_2O$ as eluent.
[e] Purified as in footnote d; $n_D^{25}$ = 1.5185.

**Table 4.** Methyl Sulfonylcyclopropanecarboxylates **4** Prepared

| Product | Reaction Time (h) | Yield[a] (%) | mp (°C) (solvent) | Molecular Formula[b] | $^1$H-NMR ($CDCl_3$/TMS) $\delta$, $J$(Hz) |
|---|---|---|---|---|---|
| **4a** | 1 | 68 | 47[c] | $C_9H_{16}O_4S$ (220.2) | 1.27 (s, 3H, $CH_3$), 1.35 (t, 3H, $J$ = 7.5, $CH_3$), 1.53 (s, 3H, $CH_3$), 2.40 (d, 1H, $J$ = 5.6, CH), 2.77 (d, 1H, $J$ = 5.6, CH), 3.00 (q, 2H, $J$ = 7.5, $CH_2$), 3.73 (s, 3H, $CO_2CH_3$) |
| **4b** | 2 | 95 | 91 (EtOH) | $C_{14}H_{18}O_4S$ (282.3) | 1.10 (s, 3H, $CH_3$), 1.20 (s, 3H, $CH_3$), 2.15 (d, 1H, $J$ = 5.9, CH), 2.68 (d, 1H, $J$ = 5.9, CH), 3.67 (s, 3H, $CO_2CH_3$), 4.23 (s, 2H, $CH_2$), 7.34 (s, $5H_{arom}$) |
| **4c** | 2 | 47 | oil[d] | $C_9H_{16}O_5S$ (236.2) | 1.26 (s, 3H, $CH_3$), 1.50 (s, 3H, $CH_3$), 2.40 (d, 1H, $J$ = 5.6, CH), 2.90 (s, 1H, OH), 3.00 (d, 1H, $J$ = 5.6, CH), 3.20 (t, 2H, $J$ = 5.5, $CH_2O$), 3.72 (s, 3H, $CO_2CH_3$), 4.05 (t, 2H, $J$ = 5.5, $CH_2SO_2$) |
| **4d** | 2 | 72 | 70 (EtOH) | $C_{13}H_{16}O_4S$ (268.3) | 1.18 (s, 3H, $CH_3$), 1.50 (s, 3H, $CH_3$), 2.48 (d, 1H, $J$ = 5.4, CH), 2.85 (d, 1H, $J$ = 5.4, CH), 3.63 (s, 3H, $CO_2CH_3$), 7.7 (m, $5H_{arom}$) |
| **4e** | 2 | 74 | 91 (EtOH) | $C_{14}H_{18}O_4S$ (282.3) | 1.18 (s, 3H, $CH_3$), 1.41 (s, 3H, $CH_3$), 2.53 (d, 1H, $J$ = 5.5, CH), 2.67 (s, 3H, $CH_3$), 2.96 (d, 1H, $J$ = 5.5, CH), 3.68 (s, 3H, $CO_2CH_3$), 7.60 (m, $4H_{arom}$) |
| **4f** | 2 | 75 | 65 (MeOH) | $C_{14}H_{18}O_4S$ (282.2) | 1.15 (s, 3H, $CH_3$), 1.50 (s, 3H, $CH_3$), 2.38 (s, 3H, $CH_3$), 2.50 (d, 1H, $J$ = 5.2, CH), 2.87 (d, 1H, $J$ = 5.2, CH), 3.63 (s, 3H, $CO_2CH_3$), 7.57 (m, $4H_{arom}$) |

[a] Yields of isolated products.
[b] Satisfactory microanalyses: C ±0.15, H ±0.44, S ±0.26.
[c] Chromatographed on a silica gel column using $Et_2O$/petroleum ether (bp 40–70°C) (1:1) as eluent.
[d] Purified as in footnote c; $n_D^{19}$ = 1.4847.




In conclusion the diastereoselective dealkoxycarbonylation of diesters **1** is a convenient method for the synthesis of substituted cyclopropanecarboxylic esters of known configuration; it might find further application in other syntheses, e.g., of intermediates bearing the easily removed sulfenyl or sulfonyl functions.

All reagents were of commercial quality from freshly opened containers. Dimethyl sulfoxide was distilled under reduced pressure before use. All melting points are uncorrected. Microanalyses were obtained on a Carlo Erba model 1106 Element analyzer. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Varian FT-80A spectrometer.

**Dimethyl 3-Alkylsulfonyl- or 3-Arylsulfonyl-2,2-dimethylcyclopropane-1,1-dicarboxylates 3; General Procedure:**

Method A: The stirred solution of the 3-alkylthio or 3-arylthio derivative[9] **1a–d** (15 mmol) in MeOH (30 mL) are added 35% $H_2O_2$ (9 mmol) and $(NH_4)_2MoO_4$ (10 mg), and the mixture is refluxed for 20 h. It is then poured into brine (50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The extract is dried ($Na_2SO_4$) and evaporated. The solid residue is crystallized from an appropriate solvent (see Table 3).

Method B: A mixture of the 3-arylthio derivative **1e,f** (15 mmol), 35% $H_2O_2$ (75 mmol), and AcOH (50 mL) is refluxed for 1 h, then poured into $H_2O$ (50 mL). The resultant mixture is extracted with $CHCl_3$ (3 × 50 mL). The organic layer is washed with 10% aq $NaHCO_3$ (3 × 50 mL), dried ($Na_2SO_4$), and evaporated. Product **3e** is column chromatographed on silica gel using $Et_2O$ as eluent; product **3f** is crystallized from MeOH.

**Dealkoxycarbonylation of Cyclopropane-1,1-dicarboxylic Esters 1 and 3; General Procedure:**

A mixture of the ester **1** or **3** (8 mmol), NaCl (0.47 g, 8 mmol), DMSO (25 mL), and $H_2O$ (1.8 mL) is refluxed for the time given in Tables 2 or 4 (until $CO_2$ evolution ceases). It is then poured into $H_2O$ (50 mL) and extracted with $Et_2O$ (3 × 50 mL). The extract is dried ($Na_2SO_4$) and evaporated to give the crude product **2** or **4**. The sulfides **2** are purified by column chromatography on silica gel using $Et_2O$/petroleum ether (bp 40–70 °C) (1:1) as eluent; the sulfones **4** are crystallized from EtOH.

**1-Methoxycarbonyl-2,2-dimethyl-3-phenylthiocyclopropanecarboxylic Acid (5):**

To a stirred solution of diester **1d** (2.9 g, 10 mmol) in MeOH (30 mL) is added KOH (1.3 g, 23 mmol) and the mixture is refluxed for 6 h. After cooling and acidification with 10% aq HCl (10 mL), the mixture is extracted with $CHCl_3$ (3 × 30 mL) and dried ($Na_2SO_4$). Evaporation of the solvent affords 1.7 g of the carboxylic acid **5** (1.7 g) which is purified by crystallization from toluene/petroleum ether (bp 40–70 °C); yield: 1.6 g (63%); mp 117–118 °C.

$C_{14}H_{16}O_4S$ (280.3) calc. C 59.99 H 5.75 S 11.43; found 59.31 5.57 11.65

$^1$H-NMR ($CDCl_3$/TMS): $\delta$ = 1.34 (s, 3H, $CH_3$), 1.38 (s, 3H, $CH_3$), 3.17 (s, 1H, CH), 3.66 (s, 3H, $CO_2CH_3$), 7.20 (s, 5H$_{arom}$), 8.90 (s, 1H, $CO_2H$).

**2,2-Dimethyl-3-phenylthiocyclopropane-1,1-dicarboxylic Acid (6):**

A mixture of diester **1d** (2.9 g, 10 mmol) and 10% aq KOH (50 mL) is stirred at 40 °C for 20 h. The solution is then acidified with 10% aq HCl (35 mL), and extracted with $Et_2O$ (3 × 50 mL). The $Et_2O$ layer is shaken with 10% aq $NaHCO_3$ (3 × 50 mL), the aq $NaHCO_3$ extract is acidified with 10% aq HCl and extracted with $Et_2O$ (3 × 50 mL). This latter $Et_2O$ extract is dried ($Na_2SO_4$) and evaporated to give **6** as a solid (2 g) which is recrystallized from toluene/light petroleum; yield: 1.9 g (75%); mp 125–127 °C.

$C_{13}H_{14}O_4S$ (266.3) calc. C% 58.64 H% 5.30 S% 12.04; found 58.54 5.26 12.30

$^1$H-NMR (DMSO-$d_6$/TMS): $\delta$ = 1.35 (s, 6H, $CH_3$), 3.12 (s, 1H, CH), 7.20 (s, 5H$_{arom}$), 7.90 (s, 2H, $CO_2H$).

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