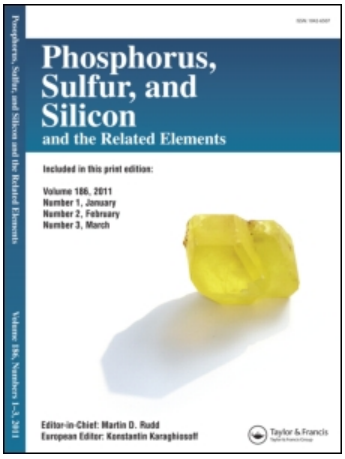


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# PTC SULFANYLATION OF SOME CARBOXYLIC ACIDS DERIVATIVES ACTIVATed BY α-SULFONYL OR α-SULFINYL GROUP, In SOLID-LIQUID SYSTEM

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# PTC SULFANYLATION OF SOME CARBOXYLIC ACIDS DERIVATIVES ACTIVATED BY α-SULFONYL OR α-SULFINYL GROUP, IN SOLID-LIQUID SYSTEM*

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The sulfanylation of α-sulfonyl substituted lactone and thioesters and α-sulfinyl-substituted esters and thioesters, employing solid $K_2CO_3$, S-methyl methanethiosulfonate and TEBA, is reported. The results are compared with those in the homogeneous phase and in the non-catalytic two-phase system.

*Keywords:* PTC sulfanylation; α-sulfonylbutyrolactone; α-sulfonyl thioesters; α-sulfinyl esters; α-sulfinyl thioesters.

## INTRODUCTION

Alkali carbonates have been shown to be sufficiently strong bases to generate carbanions from such weak carbon acids as malonates, α-keto and α-cyano esters, benzonitrile, α-diketones etc., in solid-liquid two-phase systems, which were reported to undergo PTC alkylations,[1] aldolic condensations[2,3] and Michael additions.[4–6] Recently,[7] we showed that this method can be also applied to sulfanylation of α-sulfonyl esters **1**, which, by reaction with S-methyl methanethiosulfonate, in the presence of solid $K_2CO_3$ and catalytic amount of TEBA at r.t.,

* Dedicated to Professor Robert Wolf on the occasion of his 70th birthday.

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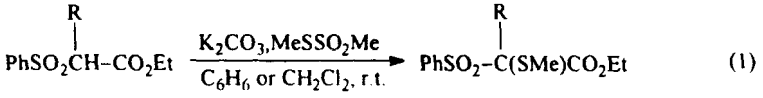
afforded the corresponding mono-sulfanylated derivatives **2** in 75–96% yields (Equation 1).



(1)

The superiority of this method over the conventional homogeneous one became evident upon comparison with the reactions in which NaH/DMSO was employed as base and afforded the sulfanylated products in much lower yields. The fact that very low yield of the sulfanylated derivative (~6%) was obtained using solid $K_2CO_3$, but in the absence of TEBA, indicated strongly the important role of the phase transfer step in these reactions.

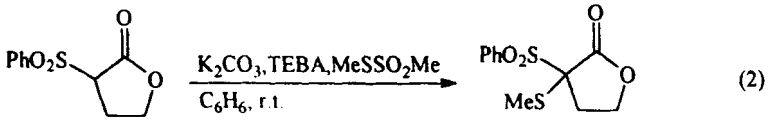
In this communication the PTC sulfanylation is extended to other activated carboxylic acids derivatives, such as α-sulfonyl lactone, α-sulfonyl thioesters as well as α-sulfinyl ester and α-sulfinyl thioester.



## RESULTS AND DISCUSSION

### 1. α-Sulfonyl lactone and α-sulfonyl thioesters.

When α-sulfonyl-γ-butyrolactone **3** was submitted to reaction with solid $K_2CO_3$, in the presence of TEBA, employing S-methyl methanethiosulfonate as sulfenylating agent at r.t., the corresponding α-sulfanylated derivative **4** was obtained in a yield of 78% (Equation 2). However, it was verified that in this case the sulfanylation occurs also in the absence of TEBA to give the derivative **4** in the same yield. This result disagrees with that for the α-sulfonyl esters, which in non-catalytic condition was shown to be practically unreactive.[7]



(2)

It seems reasonable to admit that, similar to the mechanism proposed for PTC alkylation of the active methylene compounds,[8] three main steps would occur in the PTC sulfanylation: (1) deprotonation with $K_2CO_3$ at the interface of the solid-liquid, (2) formation of a lipophilic ion-pair between carbanion and catalyst and migration to the organic phase, and (3) sulfanylation of the ion-pair with regeneration of the catalyst. It may be also suggested that in the absence of a cat-

alyst, in the case of the very active anionic species, the sulfanylation could occur at the interface. In the case of the α-sulfonyl-γ-butyrolactone, this increase of reactivity could be due to the formation of the strained cyclic enolate.

Contrary to the sulfanylation of α-sulfonyl ketones, which has received much attention,[9] no interest was found in the literature for sulfanylation of α-sulfonyl thioesters. This fact, as well the possibility of further thermal decomposition of the monosulfanylated derivatives[10,11] which would lead to α-ketothioesters of biological interest,[12] compelled us to undertake the sulfanylation studies of some α-sulfonyl thioesters. Initial investigations in homogeneous phase, using NaH/DMSO, showed that although S-methyl methanethiosulfonate is an appropriate sulfanylating agent for the α-sulfonyl thiopropionate **5a** to give sulfanylated derivative **6a** (89%), it fails in the case of α-sulfonylthioacetate **5c**, leading instead to a complex mixture and starting material. However, good yields of the sulfanylated products **6b,c** were obtained employing N-methylthiophthalimide as sulfanylating agent (Table I).

TABLE I Sulfanylation reactions of some a-sulfonyl thioesters in homogeneous phase, at r.t., employing NaH/DMSO

| $MeO_2S-CH(R')-COSEt$ **5** R' | | Sulfenylating agent | $MeO_2S-C(SMe)(R')COSEt$ **6** % Yields[a] |
|---|---|---|---|
| a | Me | $MeSO_2SMe$ | 89 |
| b | H | Phthal N-SMe | 60 |
| c | Bz | Phthal N-SMe | 53 |

a. Isalated yield.

In fact, α-sulfanylated derivatives **6a,c** underwent thermal decomposition to give the corresponding α-keto thioesters **7a,c** in yields of 75 and 51%, respectively (Equation 3 and 4). It is noteworthy that the use of a much lower temperature for decomposition of the benzylic derivative **6c** is in accord with the ionic mechanism proposed for this thermal rearrangement.[10,11]

$$\underset{\textbf{6a}}{MeO_2S-C(SMe)(Me)COSEt} \xrightarrow{160^oC} \underset{\textbf{7a}}{MeCOCOSEt} \qquad (3)$$

$$\underset{\textbf{6c}}{MeO_2S-C(SMe)(Bz)COSEt} \xrightarrow{80^oC} \underset{\textbf{7c}}{BzCOCOSEt} \qquad (4)$$

The sulfanylation of a serie of α-sulfonyl thioesters **5a',b',d,e** in the solid-liquid catalytic two-phase system, using $K_2CO_3$, S-methyl methanethiosulfonate and TEBA afforded the corresponding mono-sulfanylated derivatives **6a',b',d,e** in good yields (Table II). However, the sulfanylation may also occur in the absence of TEBA, as shown by the α-sulfonyl thioesters **5a',b'**, which, when treated with sulfanylating agent, in the presence of $K_2CO_3$ in $CH_2Cl_2$, afforded the corresponding sulfanylated derivatives **6a',b'** in ca. 65%. This result is in disaccord with that for the α-sulfonyl esters, which in the absence of TEBA, afforded the corresponding sulfanylated derivatives in negligible yields.[7] It seems reasonable to attribute this increase of reactivity in the case of α-sulfonyl thioesters to the increase of acidic character of the α-methylenic group due to larger withdrawing effect of the thioester group.[13]

TABLE II Sulfanylation reactions of some a-sulfonyl thioesters, employing $K_2CO_3$, S-methyl methane thiosulfonate and TEBA in $CH_2Cl_2$, at r.t

| | R'<br>\|<br>$PhO_2S$–CHCOSMe<br>5 | R'<br>\|<br>$PhO_2S$–C(SMe)COSMe<br>6 |
|---|---|---|
| | R' | % Yields[a] |
| a' | Me | 81 |
| | | 64[b,c] |
| b' | H | 64[d] |
| | | 63[c,d] |
| d | Et | 91 |
| e | Ph | 82 |

[a]Isolated yield; [b]By g.l.c.; [c]In the absence of TEBA; [d]40°C.

## 2. α-Sulfinyl ester and thioester.

In the course of our investigations on α-sulfinyl ketones[14] we became interested in sulfanylation of the α-sulfinyl carboxylic acids derivatives. It should be mentioned that although the reactivity of α-sulfinyl esters and thioesteres has received much attention,[13,15] no sulfanylation study has been reported in the literature.

The sulfanylation results in the homogeneous phase as well by the phase transfer catalysis are shown in Table III. It may be seen that by reaction with

NaH/DMSO and S-methyl methanethiosulfonate, while α-sulfinyl thioacetate **7** afforded the corresponding sulfanylated derivative **8** in a yield of 74%, the α-sulfinyl acetate **9** gave the corresponding sulfanylated derivative **10** in only 31%. It is noteworthy that this difference in reactivity, which can be attributed to the difference in the acidity of the methylene group in ester and thioester,[13] is still observed when the sulfanylation reaction is performed using $K_2CO_3$ and TEBA. However, in both cases, **7** and **9**, the yields of the sulfanylated products **8** and **10** are low (40 and 25%, respectively). These results indicate that the first step of the sulfanylation reaction, the formation of the anionic species in these compounds, is much slower than in the corresponding sulfonyl derivatives, this difference in reactivity being due to a decrease of the electron-withdrawing effect of the sulfinyl group in comparison with the sulfonyl group.[16]

TABLE III Sulfanylation reaction of α-sulfinyl ester and thioester using S-methyl methanethiosulfonate

| *$MeSOCH_2COX$* | | *$MeSOCH(SMe)COX$* % *Yields*[a] | |
|---|---|---|---|
| *X* | | *NaH/DMSO* | *K2CO3/TEBA/$CH_2Cl_2$* |
| 7 SEt | **8** | 74 | 40 |
| 9 OEt | **10** | 3 | 25 |

[a]Isolated yield.



## FINAL CONCLUSION

The PTC sulfanylation in the solid-liquid system is shown to be a convenient method for α-sulfonyl esters, lactone and thioesters. The simplicity of the procedure, high yields of sulfanylated derivatives, the absence of secondary products, and the use of such weak base as $K_2CO_3$ makes this method more advantageous than either the traditional one in homogeneous phase or the usual PTC procedure in the liquid-liquid system, in which the use of aqueous NaOH represents a danger for hydrolysis. However, this method is not indicated for the α-sulfinyl esters and thioesters which are weaker C-H acids.

## EXPERIMENTAL

Microanalyses were performed on a Perkin Elmer 2400 CHN elemental analyser. Mps were determined in a Thomas Hoover Kofler hot-stage apparatus, using a

Dynamics Optics AHT microscope. $^1$H NMR spectra were recorded on a Bruker AC–200 or a Varian T–60 spectrometers with tetramethyl silane (TMS) as external reference. GC analyses were carried out with a Hewlett Packard HP 5890, equipped with HP–1, 10 m capillary column. Gravity column chromatography was performed on Merck Kieselgel 60 (70–230 mesh).

**α-Phenylsulfonyl-γ-butyrolactone (3)**

Prepared from α-bromo-γ-butyrolactone and sodium benzenesulfinate in ethanol, by the literature procedure described for α-phenylsulfonyl esters,[7] in 77% yield, mp 116.7–118.0 °C (from ethanol/water). $^1$H NMR (δ, $CDCl_3$), 2.61–2.82 and 2.93–3.08 (m, 2 H), 4.00–4.08 (dd, 1 H), 4.31–4.54 (m, 2 H), 7.56–7.96 (m, 5 H). Anal. Calcd. for $C_{10}H_{10}O_4S$: C: 53.09, H, 4.45; found: C, 53.11, H, 4.54.

**Ethyl α-methylsulfonyl thioesters (5a,b)**

General procedure - To crude α-methylsulfonylacid chloride (120 mmol), contained in a three-necked, round-bottomed flask, fitted with a dry ice-acetone condenser, ethanethiol (180 mmol) was added dropwise under cooling (ice-common salt bath). After complete addition, the mixture was heated at 40 °C for 3 h. After pouring into cold water, the resultant mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The organic extracts were washed with aqueous $NaHCO_3$ (5%) (1 × 25 mL) and water (2 × 25 mL), dried over $MgSO_4$, and concentrated under reduced pressure, to give crude product, purified by distillation.

**Ethyl α-methylsulfonylthiopropionate (5a)**

Yield 74%, bp 123–5 °C/0.3 mm Hg. $^1$H NMR (δ, $CCl_4$), 1.31 (t, 3 H), 1.62 (d, 3 H), 2.61–3.20 (q, 2 H), 2.94 (s, 3 H), 4.05 (q, 1 H). Anal. Calcd. for $C_6H_{12}O_3S_2$: C, 36.75, H, 6.12; found: C 36.59, H, 6.13.

**Ethyl α-methylsulfonylthioacetate (5b)**

Yield 68%, mp 67–70 °C. $^1$H NMR (δ, $CCl_4$), 1.23 (t, 3 H), 2.92 (q, 2 H), 3.03 (s, 3 H), 4.10 (s, 2 H). Anal. Calcd. for $C_5H_{10}O_3S$: C, 32.95, H, 5.53; found: C, 32.89, H, 5.70.

**Ethyl α-methylsulfonyl-phenylthioacetate (5c)**

To 0.28 g (6.6 mmol) of sodium hydride (60% in mineral oil, washed three times with dry hexane), a solution of **5b** (1.0 g, 5.4 mmol) in 10 mL of dry DMSO was slowly added via syringe. After stirring for 1 h, a solution of benzyl bromide

(1.1 g, 6.0 mmol) in 5 mL of DMSO was slowly added. After stirring for 1 h, the reaction mixture was poured into an aqueous solution of $NH_4Cl$ (5%) and extracted with $CH_2Cl_2$. The organic extracts were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, to give 0.91 g (64%) of a white solid, mp 77–80 °C (ethyl acetate/hexane). $^1H$ NMR (δ, $CCl_4$), 1,16 (t, 3 H), 2.88 (q, 2 H), 3.02 (s, 3 H), 3.35–3.41 (m, 2 H), 4.08–4.13 (dd, 1 H), 7.16–7.29 (m, 2 H), 7.21–7.32 (m, 3 H). Anal. calcd. for $C_{12}H_{16}O_3S_2$: C, 52.91, H, 5.92; found: C, 52.52, H, 5.87.

**Methyl α-phenylsulfonyl-thioacetate (5b')**

To a solution of 12.6 g (80 mmol) of sodium benzenesulfinate in 100 mL of dry DMSO was added, dropwise, methyl α-bromothioacetate[17] (10 g, 60 mmol). After stirring for 5 h at r.t., the reaction mixture was poured into satd aqueous NaCl and extracted with $CH_2Cl_2$(3 × 25 mL). After washing with aqueous $Na_2S_2O_3$(2 × 25 mL) and water (2 × 25 mL) and drying over $MgSO_4$, the solvent was removed to give 11.7 g (85%) of a white solid, mp 32.7–33.8°C. $^1H$ NMR (δ, $CDCl_3$), 2.32 (s, 3 H), 4.31 (s, 2 H), 7.55–7.94 (m, 5 H). Anal. calcd. for $C_9H_{10}O_3S_2$: C, 46.94, H, 4.38; found: C, 46.95, H, 4.20.

**Methyl α-phenylsulfonylthioesters (5a',5d,5e)**

General Procedure - To the appropriate α-bromoacid (0.20 mol), it was added, dropwise at r.t., thionyl chloride (0.30 mol). The reaction mixture was heated at 40 °C for 4 h. After distillation of excess thionyl chloride, the flask was fitted with a dry ice-acetone condenser, and methanethiol (0.22 mol) was added dropwise under cooling (common ice-salt bath). After addition the mixture was stirred for 2 h at r.t. The resultant mixture was heated at 40 °C for 1 h, and then poured into water and extracted with $CH_2Cl_2$ (3 × 25 mL). After washing the organic extract with aqueous $NaHCO_3$ (5%) (1 × 25 mL), water (2 × 25 mL) and drying over $MgSO_4$, the solvent was removed under reduced pressure. The purified α-bromothioester (0.082 mol) was added, dropwise at r.t., to a solution of sodium benzenesulfinate (0.12 mol) in 150 mL of dry DMSO. After stirring for 5 h at r.t., the resultant mixture was poured into satd aqueous NaCl and extracted with $CH_2Cl_2$ (3 × 25 mL). The organic extract was washed with $Na_2S_2O_3$ (2 × 25 mL), water (2 × 25 mL) and dried over $MgSO_4$. Removal of solvent and washing of the crude product with hexane yielded pure α-sulfonylthioester.

**Methyl α-bromothiopropionate**

Yield 74%, bp 43–5 °C/1.7 mm Hg. Anal. calcd. for $C_4H_7BrOS$ : C, 26.24, H, 3.85; found: C, 26.16, H, 3.66.

**Methyl α-phenylsulfonylthiopropionate (5a')**
Yield 86%, mp 31–33.5 °C. $^1$H NMR (δ, $CDCl_3$), 1.58 (d, 3 H), 2.30 (s, 3 H), 4.20 (q, 1 H), 7.53–7.89 (m, 5 H). Anal. calcd. for $C_{10}H_{12}O_3S_2$. C, 49.16, H, 4.95; found C, 49.09, H, 4.91.

**Methyl α-bromothiobutyrate**
Yield 76%, bp 58–60 °C/2.7 mm Hg. Anal. calcd. for $C_5H_9BrOS$ requires C, 30.47, H, 4.60; found C, 30.59, H, 4.37.

**Methyl α-phenylsulfonylthiobutyrate (5d)**
Yield 72%, mp 61–2 °C. $^1$H NMR (δ, $CDCl_3$), 0.98 (t, 3 H), 1.92–2.12 (m, 2 H), 2.32 (s, 3 H), 3.99 (dd, 1 H), 7.51–7.87 (m, 5 H). Anal. calcd. for $C_{11}H_{14}O_3S_2$ : C, 51.14, H, 5.46; found C, 51.10, H, 5.37.

**Methyl α-bromo-phenylthioacetate**
Yield 73%, mp 134–140 °C. Anal. calcd. for $C_9H_9BrOS$: C, 44.10, H, 3.70; found C, 44.39, H, 3.86.

**Methyl α-phenylsulfonyl-phenylthioacetate (5e)**
The crude product was purified by recrystallization using hexane/acetone. Yield 71%, mp 139–139.5 °C. $^1$H NMR (δ, $CDCl_3$), 2.32 (s, 3 H), 5.23 (s, 1 H), 7.30–7.62 (m, 10 H). Anal. calcd. for $C_{15}H_{14}O_3S_2$ : C, 58.80, H, 4.60; found C, 58.71, H, 4.54.

**Ethyl α-methylsulfinylthioacetate (7)**
To a solution of ethyl α-methylsulfanylthioacetate (20 g, 13.3 mmol) in glacial acetic acid (3.20 g; 53.3 mmol), hydrogen peroxide (30%, 1.58 g; 46.7 mmol) was slowly added. The reaction mixture was further stirred for 1 h and $CH_2Cl_2$ (80 mL) was added, followed by solid $K_2CO_3$ (3.9 g) in small portions, under vigorous stirring. After 20 min., the suspension was filtered, and the organic layer was dried over $Na_2SO_4$. After removal of solvent, the crude product was a white amorphous solid (2.0 g; 90%) characterized by $^1$H NMR (δ, $CCl_4$, 60 MHz), 1.30 (t, 3 H), 2.67 (s, 3 H), 2.92 (q, 2 H), 3.83 (s, 2 H).

**Ethyl α-methylsulfinylacetate (9)**
Prepared from ethyl α-methylsulfanylacetate using the above described oxidation procedure. Yield 82%, bp 110 °C/1.5 mm Hg. $^1$H NMR (δ, $CCl_4$, 60 MHz), 1.30 (t, 3 H), 2.70 (s, 3 H), 3.65 (s, 2 H), 4.20 (q, 3 H).

**Sulfanylation in homogeneous phase - Method A -**

Typical Procedure - To a suspension of 0.20 g (6.0 mmol) of NaH (70% in mineral oil, washed twice with dry hexane) in 5 mL of DMSO, under $N_2$, 1.0 g (5.1 mmol) of ethyl α-methylsulfonylthiopropionate (**5a**) dissolved in 15 mL of dry DMSO, was added via seringe. Stirring was continued for 1 h and 0.65 g (5.1 mmol) of 5-methyl methanethiosulfonate was added dropwise, under continuous stirring. After 2 h, the reaction mixture was poured into satd aqueous $NH_4Cl$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 31 mL). The organic extract was washed with water (4 × 50 mL) and dried over $MgSO_4$. Removal of solvent yielded 1.1 g (89%) of 6a as an orange oil. $^1H$ NMR (δ, $CCl_4$), 1.26 (t, 3 H), 1.82 (s, 3 H), 2.31 (s, 3 H), 2.89 (q, 2 H), 3.08 (q, 3 H). Anal. calcd. for $C_7H_{14}O_3S_3$ : C, 34.70, H, 5.79; found: C, 34.74, H, 5.85.

**Method B - Typical Procedure**

To a stirred mixture of 0.60 g (3.8 mmol) ethyl methylsulfonylthioacetate (**5b**), 0.20 g (4.2 mmol) of NaH (60% in mineral oil, washed three times with dry hexane) and 15 mL of dry THF, was added, after stirring for 30 min., a solution of N-methylsulfanylphthalimide (0.66 g; 3.8 mmol) in 20 mL of dry THF. After stirring for 6 h at r.t., the reaction mixture was poured into aqueous $NH_4Cl$ (5%) and extracted with $CH_2Cl_2$(3 × 30 mL). After drying over $MgSO_4$, the organic extract was concentrated. After filtration of the suspended solid, the solvent was removed from the filtrate under reduced pressure and the oily residue was purified by column chromatography (hexane/ethyl acetate 3:2) to give 0.45 g (60%) of **6b** as a white solid, mp 44–6 °C. $^1H$ NMR (δ, $CDCl_3$), 1.27 (t, 3 H), 2.48 (s, 3 H), 3.01 (q, 2 H), 3.16 (s, 3 H), 4.47 (s, 1 H). Anal. calcd. for $C_6H_{12}O_3S_3$: C, 31.58, H, 5.26; found: C, 31.60, H, 5.40.

**Ethyl α-benzyl-α–methylsulfonyl-α-methylsulfanylthioacetate (6c)**

Prepared by method B modified using DMSO as solvent. After usual work up, **6c** was obtained as an yellow oil (53%) characterized by $^1H$ NMR (δ, $CDCl_3$), 1.22 (t, 2 H), 2.38 (s, 3 H), 2.90 (s, 3 H), 3.11 (q, 2 H), 3.42–3.51 (ds, 2 H), 7.08 (s, 5 H). This product proved to be unstable.

**Ethyl α-methylsulfinyl-α–methylsulfonylthioacetate (8)**

Prepared by method A. Yield 74%, oil (after column chromatography, acetone/hexane, 2:8). $^1H$ NMR (δ, $CCl_4$, 60 MHz), 2.34 (s, 3 H), 2.43 (s, 3 H), 2.72–2.76(ds, 3 H), 4.35 (ds, 1 H). Anal. calcd. for $C_5H_9O_2S_3$: C, 30.30, H, 5.08; found: C, 30.36, H, 5.03.

**Ethyl α-methylsulfinyl-α–methylsulfonylacetate (10)**

Prepared by method A using dimethyldisulfide as sulfanylating agent. Yield 31%, oil (after column chromatography, acetone/hexane, 2:8). $^1$H NMR (δ, $CCl_4$, 60 MHz), 1.30 (t, 3 H), 2.30 (s, 3 H), 2.60 (ds, 3 H), 4.20 (m, 3 H). Anal. calcd. for $C_6H_{12}O_3S_2$ : C, 36.73, H, 6.12; found: C, 36.85, H, 6.01.

**Sulfanylation of thioesters by PTC**

General Procedure - A mixture of α-phenylsulfonylthioester (2.0 mmol), solid $K_2CO_3$ (4.0 mmol), TEBA (10 mol %) 5-methyl methanethiosulfonate (2.0 mmol) in 6.0 mL of $CH_2Cl_2$ was stirred for 5 h.

Crude products were purified by column chromatography as described for each compound.



**Methyl α-methylsulfanyl-α–phenylsulfonylthiopropionate (6a')**

Purified by washing the crude product with hexane. Yield 81%, oil. $^1$H NMR (δ, $CDCl_3$), 1.95 (s, 3 H), 2.31 (s, 3 H), 2.41 (s, 3 H), 7.54–7.99 (m, 5 H). Anal. calcd. for $C_{11}H_{14}O_3S_3$: C, 45.49, H, 4.86; found C, 45.17, H, 4.93.

**Methyl α-methylsulfanyl-α–phenylsulfonylthioacetate (6b')**

Purified by column chromatography (diethyl ether/hexane; gradient). Yield 64%, mp 60–62 °C. $^1$H NMR (δ, $CDCl_3$), 2.36 (s, 6 H), 4.65 (s, 1 H), 7.54–7.99 (m, 5 H). Anal. calcd. for $C_{10}H_{12}O_3S_2$ : C, 43.45, H, 4.37; found C, 43.51, H, 3.98.

**Methyl α-methylsulfanyl-α–phenylsulfonylthiobutyrate (6d)**

Purified by washing the crude product with hexane. Yield 91%, mp 57–58 °C. $^1$H NMR (6, $CDCl_3$), 1.05 (s, 3 H), 2.07–2.22 (m, 1 H), 2.29 (s, 3 H), 2.37 (s, 3 H), 2.42–2.57 (m, 1 H), 7.49–7.94 (m, 5 H). Anal. calcd. $C_{12}H_{16}O_3S_3$ : C, 47.34, H, 5.30; found C, 47.10, H, 5.36.

**Methyl α-methylsulfanyl-α–phenylsulfonyl-phenylthioacetate (6e)**

Recrystallized from hexane/acetone. Yield 82%, mp 140–142.5 °C. $^1$H NMR (δ, $CDCl_3$), 2.38 (s, 3 H), 2.60 (s, 3 H), 7.19–7.61 (m, 10 H). Anal. calcd. for $C_{16}H_{16}O_3S_3$ : C, 54.52, H, 4.58; found C, 54.41, H, 4.46.

### α-Methylsulfanyl-α-phenylsulfonyl-γ-butyrolactone (4)

To 1.0 g (4.4 mmol) of α-phenylsulfonyl-γ-butyrolactone was added 15 mL of benzene, 1.28 (9.3 mmol) of $K_2CO_3$ and 0.10 g (10 mol %) of TEBAC. The resulting suspension was stirred for 1 h. After this time, a solution of 5-methyl methanethiosulfonate (5.3 mmol) in 2 mL of benzene was added and the mixture was further stirred for 1 h.

After filtration, the solid was washed with (3 × 20 mL) of $CH_2Cl_2$ and the organic filtrate washed with 50 mL aqueous $NH_4Cl$ and dried over $MgSO_4$. After removal of solvent and recrystallization of the resulting solid (ethanol/water), 0.93 g (78%) of white crystals of 4 were obtained (mp 105.8–106.7 °C). $^1H$ NMR (δ, $CDCl_3$), 2.06 (s, 1 H), 2.26–2.38 and 3.15–3.31 (m, 2 H), 4.32–4.51 (m, 2 H); 7.55–8.06 (m, 5 H). Anal. calcd. for $C_{11}H_{12}S_2O_4$: C, 48.51, H, 4.44; found: C, 48.49, H, 4.36.



### Thermal decomposition experiments

The decomposition temperatures, for compounds **6a** and **6c** were determined as follows: samples of the sulfanylated sulfonylthioesters were heated in NMR tubes in a 50 °C to 190 °C range. After each 20 °C increment, $CDCl_3$ was added to the NMR tube and formation of **7a** or **7c** was monitored by NMR. After determination of the decomposition temperature, 1.0 g samples of **6a** and **6c** were heated in a flask and the decomposition product was isolated by distillation.

### Ethyl thiopyruvate (7a)

Decomposition temperature: 160 °C. Yield 75%, bp 62–4 °C/10 mm Hg. $^1H$ NMR (6, $CCl_4$), 1.26 (t, 3 H), 2.32 (s, 3 H), 2.81 (q, 2 H). Anal. calcd. for $C_6H_8O_2S$ : C, 45.45, H, 6.06; found: C, 45.32, H, 6,15.

### Ethyl phenylthiopyruvate (7c)

Decomposition temperature: 80 °C. Yield 51%, bp 80–83 °C/0.5 mm Hg. $^1H$ NMR (δ, $CDCl_3$), 1.23 (t, 3 H), 3.02 (q, 2 H), 3.48 (s, 2 H), 7.08 (s, 5 H). Anal. calcd. for $C_{11}H_{12}O_2S$ : C, 63.46, H, 5.77; found: C, 63.29, H, 5.63.

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## *References*

[1] Fedorynski, M., Wojciechowski, K., Matacz, Z. and Makosza, M. *J. Org. Chem.*, **43**, 4682 (1978).
[2] Dehmlow, E. V. and Sharmont, A.R. *J. Chem. Research (S)*, 106 (1981).
[3] Jonczyk, A. and Owczarczyk, Z. *Synthesis*,297 (1985).
[4] Gonzalez, J., Sanchez, F. and Torres, T. *Synthesis*, 911 (1983).
[5] Chan, C. and Huang, X. Synthesis, 224 (1984).
[6] Skarzewski, J. *Synthesis*, 1125 (1990).
[7] Wladislaw, B., Marzorati, L., Claro Jr., N. F. and Di Vitta, C. *Synthesis*, in press.
[8] O'Donnell, M.Y., Shengde, W. and Hoffman, Y.C. *Tetrahedron*, **50**, 4507 (1994).
[9] Grossert, J.S. and Dubey, P.K. J. *Chem. Soc. Chem. Commun*, 1183 (1982).
[10] Wladislaw, B., Marzorati, L. and Uchôa, R. B. *Synthesis*, 964 (1986).
[11] Wladislaw, B., Marzorati, L. and Uchôa, R. B. *Phosphorus and Sulfur*, **32**, 87 (1987).
[12] Huxtable, R. I., *Biochemistry of Sulfur*,Plenum Press, New York (1986).
[13] Wladislaw, B., Marzorati, L. and Gruber, J. *Phosphorus, Sulfur and Silicon*, **47**, 23 (1990).
[14] Wladislaw, B., Marzorati, L. and Biaggio, F. C. *J. Org. Chem.*, **58**, 6132 (1993).
[15] Solladié, G. *Asymmetric Synthesis*, **vol. 2**, Part A, Acad. Press Inc., New York, 1989, p. 157–199.
[16] Oae, S. and Uchida, Y. "Behaviour of α-Sulfinyl and α-Sulfonyl Carbanions", in The Chemistry of Sulphones and Sulphoxides, Ed. S. Patai, Z. Rappoport and C. J. Stirling, John Wiley and Sons Ltd., Winchester, 1988, p. 384.
[17] Liu, H-J., Rose, P.A. and Sosaki, D. J. *Can. J. Chem.*, **69**, 934 (1991).