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Oxidation of Ketene-S,S-Acetals, Thioacetals, and Thioketals by Dimethyldioxirane: A Convenient Method for the Preparation of Bis-Sulfones

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ABSTRACT

The oxidation of a series of ketene-S,S-acetals, **2a–f**, *and a series of thioacetals and thioketals,* **4a–g**, *with a fourfold or greater excess of dimethyldioxirane,* **1**, *produced the corresponding bis-sulfones* **3a–f** *and* **5a–g** *in excellent yields. The reaction of the bis-sulfides with one, two, and three equivalents of* **1** *yielded monosulfoxides, bis-sulfoxides, and sulfoxide-sulfones, respectively, as the major products. The order of addition of the reactants as well as the temperature of the reaction mixture changed the product distributions. The use of low-temperature, rapid stirring and the addition of the dioxirane solution to the bis-sulfide maximized the yield of the major product. The results are consistent with an electrophilic oxygen-atom transfer mechanism in which the rate of sulfide oxidation is much faster than oxidation of sulfoxide to sulfone. However, sulfoxide oxidation is of a sufficient rate such that local concentration effects affect the results.*

INTRODUCTION

Dioxiranes, three-membered cyclic peroxides, are versatile, highly reactive oxygen-atom transfer reagents [1]. Dimethyldioxirane was shown by Curci et al. [2] to be the oxygen-atom transfer agent in the caroate-acetone system. Subsequent work by Murray et al. showed [3] that dialkyldioxiranes could be isolated from the peroxymonosulfate (caroate)-ketone reaction mixtures by low-temperature distillation. Dimethyldioxirane was found [3] to be an efficient, rapid oxidizing agent for the conversion of thioanisole to the sulfoxide. Furthermore, Murray et al. [4] showed that dimethyldioxirane efficiently oxidized a series of thioanisoles to the sulfoxides. Subsequent reaction of the aryl methyl sulfoxides with dimethyldioxirane resulted in rapid formation of the sulfones. Both sulfide and sulfoxide oxidation by dimethyldioxirane were found [4] to be electrophilic in character. Recently, Colonna et al. [5] have reported the enantioelective oxidation of sulfides by in situ generated dioxiranes. The oxidation of thianthrene 5-oxide has been employed as a mechanistic probe for assessing the nucleophilic/electrophilic character of oxygen-atom transfer reagents [6]. Early reports on this method [6a] suggested that S oxidation by dimethyldioxirane was nucleophilic in character rather than electrophilic [4,7]. However, recent results [6b], correcting an experimental oversight, have shown dimethyldioxirane to be an electrophilic reagent. We report here on the oxidation of several series of bis-sulfides by dimethyldioxirane, which shows that S oxidation is electrophilic in character, in addition, the reaction constitutes a convenient method for the preparation of bis-sulfones as well as the intermediate oxidation products.

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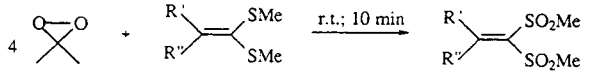
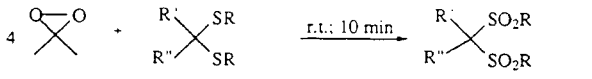
RESULTS

The reaction of four or more equivalents of dimethyldioxirane **1** in dried acetone with a series of ketene-S,S-acetals (**2a–f**, rxn 1) and a series of thioacetals and thioketals (**4a–g**, rxn 2) yielded the corresponding *bis*-sulfones **3a–f** and **5a–g** quantitatively. No epoxidation of the *bis*-sulfones (**3a–f**) of the ketene-S,S-acetals was observed when excess dioxirane was present under the reaction conditions. In addition, no carbonyl-containing side compounds were found for the oxidation of either series of compounds **2a–f** or **4a–g**. The crude products were of high purity. Recrystallization yielded analytically pure samples in excellent yields.



1 **2a** R' = n-Pr, R'' = H **3a-f**
b R' = n-Pr, R'' = Me
c R' = Ph, R'' = H
d R' = Ph, R'' = Me
e R' = R'' = Ph
f R', R'' = $(CH_2)_5$

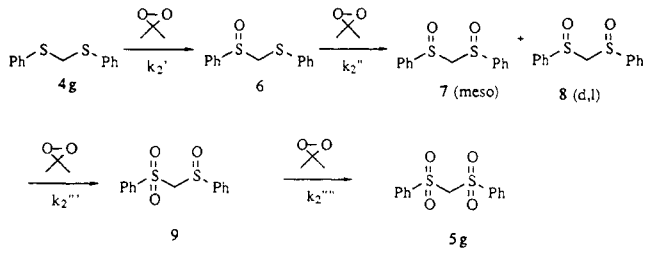
(1)



1 **4a** R, R = $(CH_2)_2$; R' = n-Pr, R'' = H **5a-g**
b R, R = $(CH_2)_2$, R' = R'' = Me
c R = R = Et; R' = R'' = H
d R = R = Et; R' = Me, R'' = H
e R = R = Et; R' = Ph; R'' = H
f R = R = Et; R' = R'' = Me
g R = R = Ph; R' = R'' =H

(2)

When *bis*-sulfides **2a–f** and **4a–g** were treated with one, two, or three equivalents of dimethyldioxirane (under inert atmosphere at ambient temperature), mixtures of mono- and bis-sulfoxides, sulfoxide-sulfones, and/or bis-sulfones were obtained (Table 1). The major product in each case corresponded to the oxidation product expected based on the number of equivalents of dioxirane. The results for oxidation of bis-sulfide **4g** are characteristic of the two series (Scheme 1). The reaction of **4a** with one equivalent of dioxirane produced the monosulfoxide **6** as the major product as well as significant amounts of bis-sulfoxides **7** and **8**. The quantity of recovered starting material, **4g**, found after reaction of one equivalent of **1**, corresponded to the total yield of the bis-sulfoxides **7** and **8**. The use of two equivalents of dioxirane produced bis-sulfoxides **7** and **8** as the major products, with monosulfoxide **6** and the sulfoxide-sulfone **9** as the minor products. The reaction of **4g**



SCHEME 1

with three equivalents of **1** yielded sulfoxide-sulfone **9** in moderate yield as well as minor amounts of **7**, **8** and bis-sulfone **5g**. Addition of one equivalent of dioxirane **1** to a pure sample of monosulfoxide **6** yielded a product distribution essentially identical to that for the addition of two equivalents of **1** to the bis-sulfide **4g**. Oxidation of **6** by **1** produced the meso bis-sulfoxide **7** in higher yield than the d,l isomer **8**. The reverse addition experiment in which solutions of **6** are added to **1** yielded important observations. More starting material, **4g**, was recovered and the distribution of the oxidation product mixture reflected a higher degree of over-oxidation under these conditions. Moreover, repetition of the one- and two-equivalent addition experiments of **1** to **4g** at −78°C yielded the appropriate oxidation product(s) in higher yield with lesser amount of side products. No sulfide-sulfone was detected (by comparison with authentic sample) in any of the dioxirane oxidations of the bis-sulfide **4g** or monosulfoxide **6**. The major products were isolated and identified by comparison with authentic samples. The results are tabulated in Table 2.

The effects of concentration and order of addition of reagent were also observable in the oxi-

TABLE 1 Bis-Sulfone Product Yields for the Oxidation of Bis-Sulfides **2a–f** and **4a–g** by Dimethyldioxirane **1** in Acetone[a]

Compound	*R*	*R'*	*R''*	*Bis-Sulfone*	*Yield %*[b]
2a	—	^{n}Pr	H	**3a**	92
2b	—	^{n}Pr	Me	**3b**	95
2c	—	Ph	H	**3c**	92
2d	—	Ph	Me	**3d**	95
2e	—	Ph	Ph	**3e**	97
2f	—	$-(CH_2)_5-$		**3f**	98
4a	$(CH_2)_2$	H	H	**5a**	93
4b	$(CH_2)_2$	H	Me	**5b**	92
4c	Et_2	H	H	**5c**	91
4d	Et_2	H	Me	**5d**	95
4e	Et_2	H	Ph	**5e**	97
4f	Et_2	Me	Me	**5f**	98
4g	Ph_2	H	H	**5f**	96

[a]Four equivalents, ambient temperature.
[b]Isolated product.

TABLE 2 Product Yields for the Oxidation of Bis(phenylthio)methane **4g** with Varying Equivalents of Dimethyldioxirane **1** in Dried Acetone

Molar Equivalent Dioxirane to Compound	*Yield 4 g*	*Yield of 6 $PhSOCH_2SPh$*	*Yield of 7 $PhSOCH_2SOPh$ (meso)*	*Yield of 8 $PhSOCH_2SOPh$ (d,l)*	*Yield of 9 $PhSO_2CH_2SOPh$*	*Yield of Disulfone 5g*	*Temp. °C*
Number							
1.0/**4g**	14 ± 2%[a]	72 ± 4%	7 ± 1%	6 ± 1%	—	—	23
1.0/**4g**	10 ± 1%[a]	84 ± 4%	4 ± 1%	2 ± 1%	—	—	−78
2.0/**4g**	—	9 ± 1%	47 ± 4%	34 ± 2%	10 ± 1%	—	23
2.0/**4g**	—	5 ± 1%	58 ± 4%	32 ± 2%	5 ± 1%	—	−78
3.0/**4g**	—	—	5 ± 1%	10 ± 1%	79 ± 5%	6 ± 1%	23
4–5/**4g**	—	—	—	—	—	100%	23
1.0/**6**	13 ± 1%[a]	43 ± 3%	34 ± 2%	11 ± 1%	—	23	
1.0/**6**[b]	29 ± 1%[a,b]	22 ± 2%[b]	21 ± 2%[b]	27 ± 2%[b]	1%[b]	23	

[a]Recovered starting material.
[b]Reverse order of addition; sulfur compound into dimethyldioxirane solution.

dation of thioanisole **10** by dimethyldioxirane. Thioanisole is often employed as the standard to determine dioxirane concentration [1,4]. Addition of **10** to dioxirane **1** resulted in the formation of the sulfoxide **11** as the major product along with variable amounts of sulfone **12** (rxn 3).

$$\underset{10}{PhSMe} \xrightarrow{1} \underset{11}{Ph\text{-}S(O)Me} \xrightarrow{1} \underset{12}{Ph\text{-}S(O_2)Me} \qquad (3)$$

If one equivalent of the neat sulfide was added via syringe to the dioxirane solution, significant but variable yields of sulfone were obtained. If the solution was not stirred, even with rapid injection of **10**, sulfone yields between 20–45% were found. Rapid stirring tended to reduce the yield of sulfone to less than 10% as did use of an approximately twofold excess of thioanisole. However, only traces of sulfone **12** were observed when the dioxirane solution was added to a solution of **10** with rapid stirring. Representative results are listed in Table 3.

DISCUSSION

Sulfones are of special interest in synthetic organic chemistry, since many useful transformations can be achieved from them [8]. The bis-sulfones of ketene-S,S-acetals have been used as the synthetic equivalent of substituted acetylenes or ethylenes in Diels–Alder and dipolar cycloaddition reactions [9a], as well as adducts for Michael additions [9b]. The bis-sulfones of thioacetals and thioketals can be used as protecting groups for ketones and aldehydes when an acid-sensitive moiety has been introduced, since the bis-sulfones can be decomposed under alkaline conditions in the presence of oxygen to regenerate the carbonyl compound [10]. A variety of oxidizing agents are known for the conversion of the sulfides into the sulfones [11], but they require drastic conditions and/or extensive workup. The results show that dimethyldioxirane (two equivalents/sulfur) oxidation of the bis-sulfides is a fast, convenient method for the preparation of bis-sulfones of ketene-S,S-acetals, thioacetals, and thioketals under mild, neutral conditions. In all cases, the yields were essentially quantitative. The crude bis-sulfones were of a high degree of purity. The use of lesser equivalents of dioxirane on the bis-sulfides is a useful method for the preparation of intermediate oxidation products in moderate yields. The method offers the advantage

TABLE 3 Representative Product Yields[a] for the Oxidation of Thioanisole **10** by Dimethyldioxirane **1** in Acetone under Conditions of Varying Concentration and Order of Addition at Ambient Temperature

Dioxirane Concentration (Initial)	*Thioanisole Concentration (Initial)*	*% Recovered **10**[a]*	*Yield % Sulfoxide **11**[a]*	*Yield % Sulfone **12**[a]*	*Comment*
0.103	0.128	34	50	15	injection of neat **10** into **1**
0.072	0.113	37	53	5	injection of neat **10** into **1**
0.103	0.246	56	41	3	injection of neat **10** into **1**
0.018	0.034	48	45	7	**10** in CH_2Cl_2 into **1**
0.022	0.034	36	65	trace	**1** into **10** in CH_2Cl_2

[a]Results will vary depending on rate of stirring and speed of addition. However, data are always internally consistent.

that, after removal of solvent, the only side products are over- or underoxidized derivatives of the starting material.

The data (Table 2) for oxidation of bis-sulfide **4g** with **1** are consistent with an electrophilic oxidation. A relative ordering of the rate constants (Scheme 1) $k_2' > k_2'' > k_2''' > k_2''''$ would be consistent with product studies. No traces of sulfide-sulfone were found under the reaction conditions, regardless of the number of equivalents of dioxirane added. This clearly shows that dioxirane oxidation of monosulfoxide **6** occurs exclusively on the sulfide group to yield the bis-sulfoxides **7** and **8**. The data also show that **7** and **8** are not formed at the same rate. The formation of the meso compound **7** during dioxirane oxidation of **6** is favored. Dioxirane oxidation of the bis-sulfoxides **7** and **8** to sulfoxide-sulfone **9** indicates that **7** undergoes the conversion faster than **8**. All the results are consistent: sulfide oxidation is faster than sulfoxide oxidation.

The 1,3-dioxyl diradical of **1** had been suggested [6] as the actual oxidizing agent for thianthrene 5-oxide oxidation based on an uncorrected χ_{SO} value. However, the corrected χ_{SO} value of 0.13 at 0°C [6b] is in agreement with an electrophilic oxygen-atom transfer process. In addition, dioxirane thermolysis and C–H insertion reactions, which have been postulated [12] to involve 1,3-dioxyl diradical intermediates, are much slower than S oxidation. These results appear to rule out the involvement of diradical species in S oxidation. The results for epoxidation of alkenes and α,β-unsaturated ketones by dimethyldioxirane [7] clearly showed the reagent to be electrophilic in character. Rho values determined by Murray et al. [4] were indicative of electrophilic character for both sulfide and sulfoxide oxidation. The present data show that dimethyldioxirane S oxidation is clearly electrophilic with little or no nucleophilic character. All sets of results are in agreement.

EXPERIMENTAL

All solvents were either of spectral or HPLC grade (Aldrich). Caroate (OXONE-Aldrich) was used without further purification. Ketene-S,S-acetals were prepared by published procedures: **2a** [13], **2b** [14], **2c** [15], **2d** [16], **2e** [17], and **2f** [18]. Thioanisole was available commercially (Aldrich) and was used with further purification. Authentic samples of methyl phenyl sulfoxide **11** and sulfone **12** were obtained from Aldrich. The 1,3-bis-sulfides **4a–g** were prepared by standard procedures. Sulfide-sulfoxide **6** [19a], the bis-sulfoxides **7** and **8** [19b], the sulfoxide-sulfone **9** [19a,19c], and the bis-sulfone **5g** [19d] have been previously reported. The sulfide-sulfone [19c] of **4g** was prepared via reduction of the sulfoxide-sulfone **9**. Melting points were recorded on a Thomas–Hoover (Uni-melt) capillary melting point apparatus and are uncorrected. Infrared spectra were determined with Perkin–Elmer 457-A and 1750-FT spectrophotometers. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 and on JEOL GX-270 spectrometers, with TMS as internal standard, at 200 and 50.3 MHz, respectively. The GC–MS spectra were obtained on Hewlett–Packard 5971 and 5988-A (MS) and 5890 (GC) on Finnigan MAT ITD 800 (MS) and Varian 3400 (GC) instruments, at 70 eV. Elemental analyses were performed at Instituto de Quimica, USP and at Atlantic Microlab, Inc., Atlanta, GA.

Dimethyldioxirane (**1**). Dimethyldioxirane (**1**) was prepared by the general method developed by Murray and Jeyaraman [3a]. The acetone solutions of **1** were dried over anhydrous Na_2SO_4, filtered, and stored at −17°C over fresh, anhydrous Na_2SO_4 until needed. The concentration of **1** was determined as follows: 1.50 mL of dioxirane stock solution was added to 20 μL of methyl phenyl sulfide (thioanisole) in 2 mL of acetone or methylene chloride at room temperature with rapid stirring. After 1 minute, the acetone was removed under reduced pressure. The reaction products were methyl phenyl sulfoxide (major) and methyl phenyl sulfone (trace, varying amounts). Integration of the product's methyl signals vs. those of the methoxy group of 2-bromoanisole and the methine group of triphenylmethane (added internal standards) was used to determine the yield of oxygen-atom transfer products and to calculate $[\mathbf{1}]_O$. All glassware used for dioxirane preparation had been pretreated with boiling aqueous Na_2EDTA, followed by an acetone rinse. No difficulties have been encountered in the preparation, handling, and storage of dimethyldioxirane. However, normal precautions associated with the handling of peroxides should be followed.

General Procedure for Preparation of bis-Sulfones

The appropriate quantity (four–five equivalents) of a dimethyldioxirane solution (~0.1 M) in acetone was added to 0.50 mmol of substrate in 2.0 mL of acetone, at room temperature with rapid stirring. After 10 minutes, the solvent was removed under reduced pressure to yield the bis-sulfone, which was crystallized from $CHCl_3$/hexane to yield analytically pure sample.

3a: mp 56–57.5°C. Anal. calcd for $C_7H_{14}O_4S_2$: C, 37.15; H, 6.23; S, 28.33. Found: C, 37.04; H, 6.22; S, 28.25. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.67 (t, 1H), 3.27 (s, 3H), 3.24 (s, 3H), 2.84 (q, 2H), 1.63 (st, 2H), 1.02 (t, 3H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 161.0, 142.4, 45.8, 44.4, 31.4, 22.4, 14.4. MS (70 eV) *m/z* 226 (M^+, 6.1), 211 (18.7), 185 (28.5), 147 (100.0), 81 (26.6), 67 (40.5).

3b: mp 78–79°C. Anal. calcd for $C_8H_{16}O_4S_2$: C, 39.38; H, 6.71; S, 26.68. Found: C, 39.88; H, 6.73;

S, 26.59. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.28 (s, 3H), 3.26 (s, 3H), 2.76 (t, 2H), 2.47 (s, 3H), 1.67 (st, 2H), 1.03 (t, 3H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 173.5, 138.9, 45.6, 45.2, 40.9, 24.7, 22.6, 14.3. MS (70 eV) m/z 240 (M^-, 1.2), 225 (9.7), 199 (4.4), 161 (100.0), 81 (79.4), 63 (28.1), 53 (41.7), 41 (59.3).

3c: mp 130–131°C. Anal. calcd for $C_{10}H_{12}O_4S_2$: C, 46.12; H, 4.65; S, 24.63. Found: C, 46.16; H, 4.61; S, 24.72. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.43 (s, 1H), 7.68–7.60 (m, 2H), 7.55–7.40 (m, 3H), 3.37 (s, 3H), 3.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 152.7, 140.7, 132.1, 131.5, 129.8, 128.6, 45.3, 44.1. MS (70 eV) m/z 260 (M^-, 9.0), 181 (100.0), 102 (41.5), 89 (20.5), 76 (11.2), 40 (14.8).

3d: mp 161–162°C. Anal. calcd for $C_{11}H_{14}O_4S_2$: C, 48.15, H, 5.14, S, 23.37. Found: C, 48.04, H, 5.09, S, 23.43. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.46–7.39 (m, 3H), 7.22–7.15 (m, 2H), 3.37 (s, 3H), 3.23 (s, 3H), 2.69 (s, 3H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 170.4, 141.6, 141.4, 130.0, 129.0, 126.3, 47.1, 45.8, 28.8. MS (70 eV) m/z 274 (M^-, 0.3), 195 (100.0), 115 (82.2), 103 (23.9), 40 (28.1).

3e: mp 254–256°C. Anal. calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.79; S, 19.06. Found: C, 56.90; H, 4.80; S, 18.95. ^{1}H NMR (DMSO-d_6, 200 MHz) δ 7.44–7.35 (m, 6H), 7.31–7.25 (m, 4H), 3.40 (s, 6H). ^{13}C NMR (DMSO-d_6, 50.3 MHz) δ 167.3, 141.8, 140.0, 129.9, 128.3, 128.1, 46.6. MS (70 eV) m/z 336 (M^-, 3.9), 256 (35.4), 178 (100.0), 105 (26.0).

3f: mp 155–157°C. Anal. calcd for $C_9H_{16}O_4S_2$: C, 42.84; H, 6.39; S, 25.42. Found: C, 42.80; H, 6.37; S, 25.34. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.29 (s, 6H), 3.02–2.96 (dd, 4H, J = 6.17 Hz), 1.96–1.84 (m, 4H), 1.76–1.62 (m, 2H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 178.7, 137.4, 46.3, 35.7, 29.8, 25.5. MS (70 eV) m/z 252 (M^+, 0.3), 173 (65.6), 91 (100.0), 77 (43.3).

5a: mp 196–197°C. Anal. calcd for $C_3H_6O_4S_2$: C, 21.17; H, 3.55. Found: C, 21.27; H, 3.50. ^{1}H NMR (DMSO-d_6, 200 MHz) δ 4.98 (s, 2H), 4.01 (s, 4H). ^{13}C NMR (DMSO-d_6, 50.3 MHz) δ 65.0, 52.8. MS (70 eV) m/z 170 (M^+, 35.0), 78 (100.0), 64 (42.7), 50 (33.1). IR (film) 1324 and 1180 cm^{-1}.

5b: mp 183–185°C. Anal. calcd for $C_5H_{10}O_4S_2$: C, 30.31; H, 5.09. Found: C, 30.25; H, 5.18. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.62 (s, 4H), 1.70 (s, 6H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 71.8, 48.2, 18.6. MS (70 eV) m/z 198 (M^-, 0.5), 182 (28.4), 124 (63.6), 90 (32.5), 76 (100.0), 59 (56.9). IR (film) 1307 and 1057 cm^{-1}.

5c: mp 100–101.5°C. Anal. calcd for $C_5H_{12}O_4S_2$: C, 29.92; H, 6.04. Found: C, 30.05; H, 5.79. ^{1}H NMR (acetone-d_6, 200 MHz) δ 4.97 (s, 2H), 3.44 (q, 4H), 1.38 (t, 6H). ^{13}C NMR (acetone-d_6, 50.3 MHz) δ 67.4, 49.1, 6.1. MS (70 eV) m/z 201 (M^+, + 1; 38.7), 109 (17.7), 80 (100.0), 65 (25.54), 50 (9.1). IR (film) 1334 and 1128 cm^{-1}.

5d: mp 74–75°C. Anal. calcd for $C_6H_{14}O_4S_2$: C, 33.63; H, 6.58. Found: C, 33.64; H, 6.51. ^{1}H NMR (acetone-d_6, 200 MHz) δ 4.84 (q, 1H), 3.53 (dq, 2H, J = 13.8 and 7.0 Hz), 3.34 (dq, 2H, J = 13.8 and 7.0 Hz), 1.77 (d, 3H), 1.37 (t, 6H). ^{13}C NMR (acetone-d_6, 50.3 MHz) δ 74.2, 47.0, 8.9, 5.6. MS (70 eV) m/z 215 (M^+ + 1, 59.1), 122 (12.5), 94 (27.8), 77 (43.8), 66 (100.0), 59 (19.2). IR (KBr) 1318 and 1124 cm^{-1}.

5e: mp 133–134°C. Anal. calcd for $C_{11}H_{16}O_4S_2$: C, 47.81; H, 5.84. Found: C, 47.46; H, 5.74. ^{1}H NMR (acetone-d_6, 200 MHz) δ 7.81–7.76 (m, 2H), 7.54–7.46 (m, 3H), 6.13 (s, 1H), 3.55 (q, 4H), 1.31 (t, 6H). ^{13}C NMR (acetone-d_6, 50.3 MHz) δ 132.3, 131.1, 129.6, 126.7, 81.9, 49.2, 6.0. MS (70 eV) m/z 277 (M^+, + 1; 0.1), 183 (7.9), 107 (77.4), 105 (55.1), 89 (40.4), 79 (51.7), 77 (100.0), 63 (23.8), 51 (17.4). IR (KBr) 1329 and 1149 cm^{-1}.

5f: mp 124–125°C. Anal. calcd for $C_7H_{16}O_4S_2$: C, 36.82; H, 7.06. Found: C, 36.87; H, 6.87. ^{1}H NMR (acetone-d_6, 200 MHz) δ 3.47 (q, 4H), 1.75 (s, 6H), 1.36 (t, 6H). ^{13}C NMR (acetone-d_6, 50.3 MHz) δ 81.9, 44.6, 17.3, 5.2. MS (70 eV) m/z 229 (M^- + 1, 50.8), 135 (15.6), 95 (23.7), 77 (100.0), 59 (96.2). IR (KBr) 1309 and 1149 cm^{-1}.

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