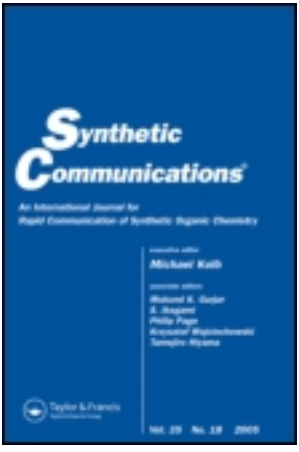

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A FACILE SYNTHESIS OF β-OXOTHIOLCARBOXYLATES FROM α-OXOKETENEDITHIOACETALS*

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A FACILE SYNTHESIS OF β-OXOTHIOLCARBOXYLATES FROM α-OXOKETENEDITHIOACETALS*

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ABSTRACT

α-Oxoketenedithioacetals and alkenoyl ketenedithioacetals underwent facile, boron trifluoride etherate assisted partial hydrolysis in dioxane to afford β-oxothiolcarboxylates and γ,δ-unsaturated β-oxothiolcarboxylates, respectively, in good yields.

α-Oxoketenedithioacetals have been shown to be highly versatile intermediates in organic synthesis.[1–3] Their reductive or alkylative 1,3-carbonyl group transpositions proceed stereoselectively to give α,β-unsaturated carboxylates and thiolcarbioxylates.[4] α-Oxoketenedithioacetals are considered as protected β-keto esters or β-ketothiolesters and can be effectively transformed to β-ketoesters by acid catalyzed solvolysis.[5,6] In this communication, we report a convenient procedure for their conversion to β-ketothiolesters. This method has been found suitable for the preparation of γ,δ-unsaturated β-ketothiolesters as well.

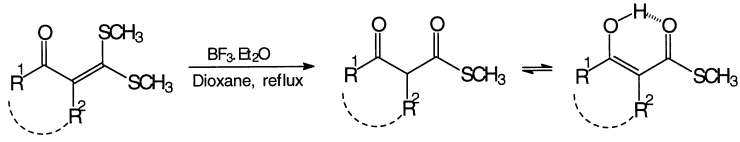
*Dedicated to the memory of Sajush.

†Corresponding author.

β-Ketothiolesters have been shown to be valuable synthons for a variety of transformations. Besides the conventional reactions of β-ketoesters,[7–9] they undergo facile transesterification reactions with various heteronucleophiles and displacement of the alkylthio group with α-hydroxy or α-amino carbonyl compounds, followed by cyclization, has been utilized in the synthesis of substituted tetronic acids and tetramic acids, including the naturally occurring fuligorubin A.[10–15] The methods currently available for the preparation of β-ketothiolesters are (i) Claisen condensation of aliphatic thiolesters;[16–19] (ii) reaction of the magnesium salt of malonic acid half thiolester with acyl imidazoles;[20] (iii) a dithiolester version of the Dieckmann condensation;[21] and (iv) the addition of sodium mercaptide to diketene.[22] The γ,δ-unsaturated β-ketothiolesters are usually prepared by the Wadsworth-Emmons coupling reaction of t-butyl-4-diethylphosphono-3-oxobutanethioate with aldehydes or ketones.[23] They are analogues of Nazarov reagents, which are valuable four-carbon components in Robinson annulation type reactions.[24–27]

The benzoyl ketenedithioacetal **1a** derived from acetophenone was treated in non-nucleophilic solvents with different Lewis and protic acids in the presence and absence of mercury salts. The methyl benzoyl thiolacetate **2a** was formed in low yield under most of these conditions. However, refluxing **1a** in dioxane in the presence of an equivalent amount of boron trifluoride etherate for 4–5 h in dioxane followed by treatment with water gave the thiolester **2a** in 52% yield.

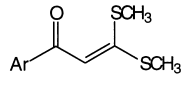
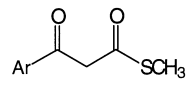
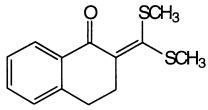
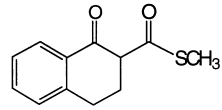
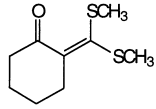
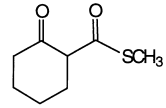
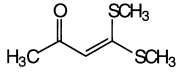
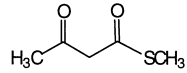
Similarly, other substituted benzoyl ketenedithioacetals **1b–e** also gave the substituted benzoyl thiolacetates **2b–e** in moderate to good yields (Scheme 1, Table 1). The ketenedithioacetal **1f** prepared from 2-acetylthiophene gave the corresponding thiolester **2f** in 48% yield. Ketenedithioacetal derived from cyclic ketones also underwent smooth conversion to the respective β-ketothiolesters. Thus, the ketenedithioacetal **1g** derived from α-tetralone gave the thiolester **2g** in nearly quantitative yield. The ketenedithioacetal **1h** prepared from cyclohexanone gave a complex product mixture under these conditions. Nevertheless, moderate yield of the thiolester **2h** was obtained on treatment of 1 h with BF_3Et_2O in dioxane at 25°C



1 2

Scheme 1.

Table 1. β-Oxothiolcarboxylates 2 Prepared

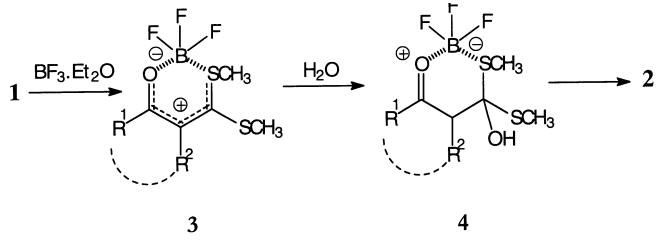
1,2	Substrate	Product	Yield (%)[a]
			
a	Ar = C_6H_5		52
b	4-$CH_3C_6H_4$		58
c	4-ClC_6H_4		90
d	$CH_3OC_6H_4$		48
e	4-BrC_6H_4		59
f	2-thienyl		48
g			97
h			64[b]
i			35

[a]Yield of the isolated product; [b]reaction was carried out at 25°C.

for 6 h, followed by work-up with water. The acetyl ketenedithioacetal **1i** also gave the methyl acetothiolacetatae **2i** in 35% yield when the reaction was carried out at 25°C.

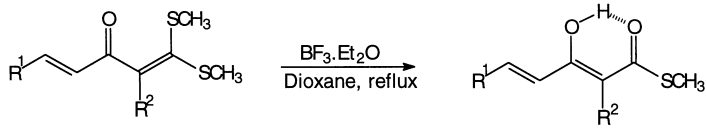
The acid-catalyzed partial hydrolysis of ketenedithioacetals involves a partially reversible protonation of the carbon-carbon double bond, followed by hydration of the intermediate dithiocarbocation formed.[28–32] The Lewis-acid assisted partial hydrolysis of acyl ketenedithioacetals could involve the initial formation of a complex **3** with borontrifluoride etherate. Addition of water to this complex during work-up to give **4**, followed by loss of methylthio group, would lead to the formation of β-oxothiolester **2** (Scheme 2).

We have extended the scope of this reaction to the preparation of γ,δ-unsaturated β-oxothiolesters **6** as well (Scheme 3). Acyl ketenedithioacetals derived from aliphatic ketones such as acetone and ethyl methyl ketone on Claisen-Schmidt condensation with aromatic aldehydes afford 5-aryl-1,1-bis(methylthio)-3-oxo-1,4-pentadienes **5** in good yields.[33,34] When the cinnamoyl ketene dithioacetal **5a** was refluxed in dioxane, in the presence of boron trifluoride etherate, the methyl cinnamoyl thiolacetate



3 4

Scheme 2.

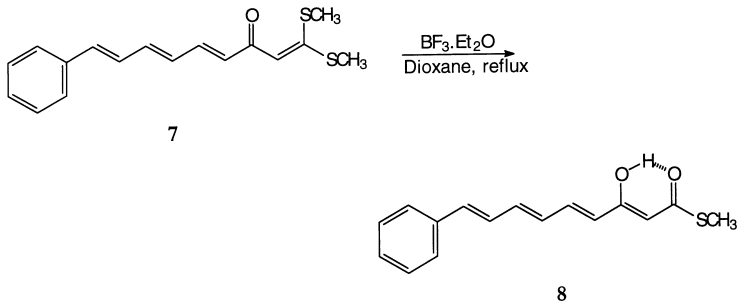


5 6

Scheme 3.

6a was formed in 87% yield. Similarly, other substituted cinnamoyl ketenedithioacetals **5b–d** also gave the respective thiolesters in good yields (Table 2). Similarly, the 1,1-bis(methylthio)-3-oxo-5-(2-thienyl)-1,4-pentadienone **5e** and the methyl substituted cinnamoyl ketenedithioacetal **5f** also gave the respective γ,δ-unsaturated β-ketoesters **6e** and **6f**.

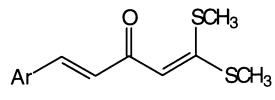
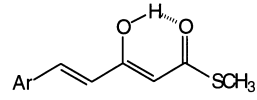
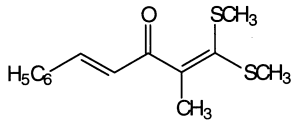
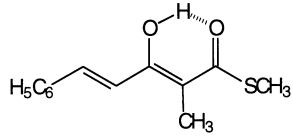
We have also examined the reaction with a polyenoyl ketenedithioacetal **7**. The Claisen-Schmidt condensation of 5-aryl-2,4-pentadienaldehyde with acetyl ketnedithioacetal gave 1,1-bis(methylthio)-3-oxo-9-phenyl-1,4,6,8-nonatetraene **7**. Treatment of **7** with borontrifluoride etherate in refluxing dioxane for 1.5 h, followed by usual work-up, gave the thiolester **8** in 88% yield (Scheme 4).



7 8

Scheme 4.

Table 2. γ,δ-Unsaturated β-oxothilesters 6 Prepared

5,6	Substrate	Product	Yield (%)
			
a	Ar = C_6H_5		87
b	4-ClC_6H_4		92
c	4-$NO_2C_6H_4$		65
d	4-$CH_3C_6H_4$		70
e	2-thienyl		90
f			67

The proton NMR spectra of β-oxothiolesters prepared indicate that they exist as a mixture of keto and enol tautomers in $CDCl_3$. γ,δ-Unsaturated β-ketothiolesters **6** and **8** exist mostly in the enol form.

In conclusion, we have developed a facile method for the partial hydrolysis of α-oxoketenedithioacetals. The method is useful for the preparation of starting from active methylene ketones in a two-step process. γ,δ-Unsaturated β-ketothiolesters and conjugated polyenoyl thiolacetates can also be prepared by this reaction in good yields.

EXPERIMENTAL

Melting points are uncorrected and were obtained on a Buch-530 melting point apparatus. IR spectra were recorded on a Schimadzu IR-470 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Jeol GX 90 or a Bruker WM 300 spectrometer with tetramethyl silane as the internal standard. MS were obtained on a Finnigen-Mat 312 instrument.

Preparation of β-Oxothiolcarboxylates 2

To the acyl ketenedithioacetal **1** (10 mmol) in dioxane (30 mL), boron trifluoride etherate (1.3 mL, 10 mmol) was added and the mixture was refluxed for 2–4 h or stirred at 25°C (in the case of **1h** and **1i**) for 6 h. The reaction mixture was then poured into cold water and was neutralized

with saturated sodium bicarbonate solution. The mixture was extracted with ether (3×50 mL) and the combined organic layer was washed with water, dried over anhydrous sodium sulphate, and the solvent removed under vacuum. The residue was column chromatographed over silica gel (60–120 mesh) using hexane-ethyl acetate(50:1) as the eluent.

S-Methyl-3-oxo-3-phenylpropanethioate(**2a**)

Obtained as a pale yellow liquid, 1 g (52%), by the reaction of the ketenedithioacetal **1a** in refluxing dioxane for 4.5 h, (keto:enol = 47:53), IR(neat); ν = 1660, 1600(C = O), 1560, 1480, 1440(C = C) 1210 cm^{-1}. ^{1}H NMR(90 MHz, $CDCl_3$) δ = 2.32(s, l.59H, SCH_3, enol), 2.40(s, 1.41H, SCH_3, keto), 4.22(s, 0.94H, CH_2, keto), 6.11(s, 0.53H, vinylic, enol), 7.20–8.10(m, 5H, arom), 13.19(s, 0.53H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) δ = 10.88(SCH_3, enol), 11.90(SCH_3, keto), 53.52(CH_2, keto), 96.87(vinylic, enol)126.92, 128.43, 128.58, 131.44, 132.67, 133.59, 135.83(arom, keto, and enol), 168.44(C-O, enol), 191.68, 192.19(C = O, keto), 194.96(C = O, enol) ppm. EIMS *m/z* l94(M^+, 7.2%), 146(49.3%), 133(11.4%), 105(100%). Anal. found C, 61.36; H, 5.10; $C_{10}H_{10}O_2S$ requires C, 61.83; H, 5.19.

S-Methyl-3-oxo-3-(4-methylphenyl)propanethioate(**2b**)

Obtained as a pale yellow liquid, 1.5 g (58%), by the reaction of the ketenedithioacetal **1b** in refluxing dioxane for 4 h, (keto:enol = 65:35), IR(neat); ν = 1678, 1600(C = O), 1580, 1565(C = C) 1215 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 2.28(s, 1.05H, SCH_3, enol), 2.34(s, 1.95H, SCH_3, keto), 2.36(s, 3H, CH_3) 4.13(s, 1.30H, CH_2, keto), 6.07(s, 0.35H, vinylic, enol), 7.07–7.28(m, 2H, arom), 7.65(d, J = 9Hz, 0.7H, arom), 7.82(d, J = 9Hz, 1.3H, arom), 13.22(s, 0.35H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) δ = 10.88(SCH_3, enol), 11.87(SCH_3, keto), 21.32, 21.47(CH_3) 53.46(CH_2, keto), 96.30(vinylic, enol), 126.26, 128.79, 129.24, 129.30, 129.84, 133.51, 142.16, 144.58(arom, keto, and enol), 168.74(C-O, enol), 191.30, 192.31(C = O, keto), 194.79(C = O, enol) ppm. EIMS *m/z* 208(M^+, 5.5%), 160(26.3%), 134(21.9%), 119(100%). Anal. found C, 63.44; H, 5.72; $C_{11}H_{12}O_2S$ requires C, 61.77; H, 5.81.

S-Methyl-3-oxo-3-(4-chlorophenyl)propanethioate(**2c**)

Obtained as a pale yellow liquid, 2 g (90%), by the reaction of the ketenedithioacetal **1c** in refluxing dioxane for 1.5 h exists as the enol form in

$CDCl_3$(> 95%), m.p. 86°–87°C, IR(KBr); $\nu = 1680$, 1625(C = O), 1560, 1535, 1480, 1440(C = C), 1390, 1210 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.39$(s, 3H, SCH_3), 6.08(s, 1H, vinylic, enol), 7.36(d, J = 9Hz, 2H, arom), 7.71(d, J = 9Hz, 2H, arom), 13.18(s, 1H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 10.88$(SCH_3, enol), 11.87(SCH_3, keto), 53.37(CH_2, keto), 96.84(vinylic, enol)127.39, 128.58, 128.79, 129.92, 131.00, 137.44(arom, keto, and enol), 166.89(C-O, enol), 194.84(C = O, enol) ppm. EIMS *m/z* 228(M^+, 13.6%), 181(74.3%), 139(100%), 111(25.8%). Anal. found C, 52.26; H, 3.90; $C_{10}H_9O_2ClS$ requires C, 52.52; H, 3.97.

S-Methyl-3-oxo-3-(4-methoxyphenyl)propanethioate(**2d**)

Obtained as a pale yellow liquid, 1g (48%), by the reaction of the ketenedithioacetal **1d** in refluxing dioxane for 6 h (keto:enol = 75:25), IR(neat); $\nu = 1650$, 1595(C = O), 1575, 1498(C = C) 1220 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.27$(s, 0.75H, SCH_3, enol), 2.34(s, 2.25H, SCH_3, keto), 3.80(s, 3H, OCH_3), 4.07(s, 1.5H, CH_2, keto), 6.05(s, 0.25H, vinylic, enol), 7.72(d, J = 9Hz, 2H, arom), 7.71(d, J = 9Hz, 2H, arom), 13.31(s, 0.25H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 10.55$(SCH_3, enol), 11.57(SCH_3, keto), 53.07(CH_2, keto), 55.04(OCH_3), 95.19(vinylic, enol), 124.43, 127.77, 128.64, 130.73 (arom, keto, and enol), 168.29(C-O, enol), 189.86, 192.19(C = O, keto), 194.22(C = O, enol) ppm. Anal. found C, 58.62; H, 5.30; $C_{11}H_{12}O_3S$ requires C, 58.85; H, 5.35.

S-Methyl-3-oxo-3-thienylpropanethioate(**2e**)

Obtained as pale yellow liquid, 0.96 g(48%), by the reaction of ketenedithioacetal **1e** in refluxing dioxane for 4 h (keto:enol = 47:53), IR(neat); $\nu = 1650$, 1615(C = O), 1540, 1420(C = C) 1215 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 2.22$(s, 2.79H, SCH_3, enol), 2.29(s, 0.21H, SCH_3, keto), 4.08(s, 1.86H, CH_2, keto), 5.95(s, 0.07H, vinylic, enol), 6.89–7.02(m, 0.07H, arom, enol), 7.02–7.09(m, 0.93H, arom, keto), 7.39–7.42(m, 0.07H, arom, enol), 7.45–7.51(m, 0.07H, arom, enol), 7.58–7.62(m, 0.93H, arom, keto), 7.67–7.78(m, 0.93H, arom, keto) ppm. ^{13}C NMR (100.4 MHz, $CDCl_3$) $\delta = 11.97$(SCH_3, keto), 54.14(CH_2, keto), 95.88(vinylic, enol)128.00, 128.24, 128.57, 130.11, 133.73, 135.15, 136.41, 142.95(arom, keto, and enol), 163.33(C-O, enol), 184.04, 191.66(C = O, keto) ppm. Anal. found C, 47.88; H, 3.97; $C_{10}H_9O_2S_2$ requires C, 47.98; H, 4.03.

S-Methyl-3,4-dihydro-1(2H)-napthalenone-2-thiocarboxylate(**2f**)

Obtained as a yellow solid, 2.14 g (97%), by the reaction of the ketenedithioacetal **1f** in refluxing dioxane for 2 h, exists as the enol form in $CDCl_3$(> 95%), m.p. 56–58°C, IR(KBr); $\nu = 3450$, 1680, 1610(C = O), 1550, 1445(C = C), 1250, 1110 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.38$(s, 3H, SCH_3), 2.52–2.95(m, 4H, CH_2), 7.08–7.35(m, 3H, arom), 7.72–7.90(m, 1H, arom), 13.40(s, 1H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 11.06$(SCH_3), 21.29, 27.62(CH_2), 61.21(CH, keto), 105.52(vinylic, enol), 126.52, 127.15, 129.51, 130.76, 138.40(arom), 162.59(C-O, enol), 196.10(C = O), 194.96 ppm. EIMS m/z 220(M^+, 34.5%), 173(100%), 145(47%), 115(90.9%), 105(60.9%). Anal. found C, 65.22; H, 5.36; $C_{12}H_{12}O_2S$ requires C, 65.37; H, 5.44.

S-Methyl cyclohexanone-2-thiolcarboxylate(**2g**)

Obtained as a pale yellow liquid, 1.10 g (64%), by the reaction of the ketenedithioacetal **1g** in refluxing dioxane for 5.5 h, exists as the enol form(> 95%) in $CDCl_3$, IR(neat); $\nu = 1620$(C = O), 1560, 1440(C = C), 1320, 1245, 1160 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 1.65$(m, 4H, CH_2), 2.26(m, 7H, SCH_3 and CH_2), 13.05(s, 1H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 10.79$(SCH_3), 21.20, 22.28, 22.43, 29.08(CH_2), 106.53(vinylic) 170.20(C-O), 196.87(C = O) ppm. Anal. found C, 55.62; H, 6.88; $C_{10}H_{10}O_2S$ requires C, 55.79; H, 7.02.

S-Methyl-3-oxo-butanethioate(**2h**)

Obtained as a pale yellow liquid, 0.46 g (35%), by the reaction of the ketenedithioacetal **1h** in dioxane at room temperature for 5.5 h, exists as the ketoform in $CDCl_3$(> 95%), IR(neat); $\nu = 1710$, 1670(C = O), 1640, 1550, 1210, 1090 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$)$\delta = 2.31$(s, 1.3H, SCH_3), 2.44 (s, 3H, CH_3, keto), 3.78(s, 2H, CH_2) ppm. ^{13}C NMR(22.4 MHz, $CDCl_3$) $\delta = 11.08$(SCH_3, enol), 11.92(SCH_3, keto), 21.42(CH_3, enol), 29.32(CH_3, keto), 58.16(CH_2, keto), 100.78(vinylic, enol), 174.98(C-O, enol), 194.23 (C = O) ppm. Anal. found C, 45.36; H, 5.93; $C_5H_8O_2S$ requires C, 45.44; H, 6.10.

Preparation of γ,δ-Unsaturated β-Oxothiolcarboxylates, 6

To the alkenoyl ketenedithioacetals **5** (10 mmol) in dioxane, boron trifluoride etherate (1.3 mL, 10 mmol) was added and the mixture was

refluxed for 2–3 h. The reaction mixture was poured into cold water, neutralized with saturated sodium bicarbonate solution, and extracted with ether(3×50 mL). The combined organic layer was washed with water, dried over anhydrous sodium sulphate, and evaporated under vacuum. The residue was column chromatographed over silica gel using hexane ethylacetate(50:2) as the eluent.

S-Methyl-3-oxo-5-phenyl-4-pentenethioate(**6a**)

Obtained as a pale yellow solid, 1.91 g (87%), by the reaction of the ketenedithioacetal **5a** in refluxing dioxane for 2 h, (keto:enol = 25:75), m.p. 56°–58°C, IR(KBr); $\nu = 3400$, 1635(C = O), 1580, 1440, 1415(C = C), 1260, 1170, 1080 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.35$(s, 3H, SCH_3), 3.91(s, 0.5H, CH_2, keto), 5.60(s, 0.75H, vinylic, enol), 6.40(d, J = 16Hz, 0.25H, vinylic, keto), 6.78(d, J = 16Hz, 0.75H, vinylic, enol), 7.18–7.63(m, 6H, arom and vinylic), 12.52(s, 0.75H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 10.64$(SCH_3, enol), 11.75(SCH_3, keto), 55.33(CH_2, keto), 101.10(vinylic, enol), 120.97, 124.73, 127.36, 128.25, 128.49, 128.61, 129.24, 130.58, 133.71, 134.85, 138.13, 144.57(arom and vinylic, keto, and enol), 165.96(C-O, enol), 190.70, 191.92(C = O, keto), 194.37(C = O, enol) ppm. ELMS *m/z* 220(M^+, 19.8%), 173(79.9%), 131(100%), 115(15.3%), 103(50.4%). Anal. found C, 65.32; H, 5.46; $C_{10}H_{10}O_2S$ requires C, 65.43; H, 5.49.

S-Methyl-3-oxo-5-(4-chlorophenyl)-4-pentenethioate(**6b**)

Obtained as a pale yellow solid, 2.30 g (92%), by the reaction of the ketenedithioacetal **5b** in refluxing dioxane for 2 h, exists in the enol form(> 95%), m.p. 122°–123°C, IR(KBr); $\nu = 1630$(C = O), 1580, 1440(C = C), 1260, 1080, 800 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.38$(s, 3H, SCH_3), 5.59(s, 1H, vinylic, enol), 6.28(d, J = 16Hz, 1H, vinylic), 7.22–7.58(m, 5H, arom and vinylic), 12.49(s, 1H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 11.00$(SCH_3), 101.64(vinylic), 121.87, 128.73, 129.06, 129.68, 133.71, 135.35, 136.96(arom and vinylic), 165.81 (C-O, enol), 194.87(C = O) ppm. EIMS *m/z* 254(M^+, 12.1%), 207(58.5%), 165(100%), 137(28.5%), 127(3.9%), 75(26.8%). Anal. found C, 56.48; H, 4.26; $C_{12}H_{11}O_2ClS$ requires C, 56.58; H, 4.35.

S-Methyl-3-oxo-5-(4-nitrophenyl)-4-pentenethioate(**6c**)

Obtained as a yellow solid, 1.73 g (65%), by the reaction of the ketenedithioacetal **5c** in refluxing dioxane for 3.5 h, exists as the enol form in $CDCl_3$(>95%), m.p. 159°–160°C, IR(KBr); $\nu = 1640$(C=O), 1600, 1515(C=C) 1340, 1260 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.35$(s, 3H, SCH_3), 5.67(s, 1H, vinylic), 6.46(d, J = 16Hz, 1H, vinylic), 7.10–8.10(m, 5H, arom and vinylic), 12.52(s, 1H, OH, enol) ppm. Anal. found C, 54.26; H, 4.10; N, 5.28; $C_{12}H_{11}NO_4S$ requires C, 54.33; H, 4.18; N, 5.28.

S-Methyl-3-oxo-5-(4-methoxyphenyl)-4-pentenethioate(**6d**)

Obtained as a pale yellow solid, 1.75 g (70%), by the reaction of the ketenedithioacetal **5d** in refluxing dioxane for 2.5 h, (keto:enol = 50:50), m.p. 82°–83°C, IR(KBr); $\nu = 1630$(C=O), 1580, 1550(C=C) 1265, 1170, 1080 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.33$(s, 3H, SCH_3), 3.69–3.71(m, 3H, OCH_3), 3.82(s, 1H, CH_2, keto), 5.51(s, 0.5H, vinylic, enol), 6.18(d, J = 17Hz, 1H, vinylic), 6.90(d, J = 9 Hz, 2H, arom), 7.28–7.58(m, 3H, arom and vinylic), 12.50(s, 0.5H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 10.70$(SCH_3, enol), 11.84(SCH_3, keto), 55.42(OCH_3), 55.56(CH_2, keto), 100.48(vinylic, enol), 118.56, 122.55, 126.43, 127.69, 129.03, 130.16, 138.04, 144.63, 166.68(arom and vinylic, keto and enol), 160.68(C-O, enol), 190.70(C=O, keto), 194.25(C=O, enol) ppm. EIMS *m/z* 250(M^+, 27.4%), 203(64.1%), 161(100%), 133(41.2%), 131(8%). Anal. found C, 62.28; H, 5.55; $C_{13}H_{14}O_3S$ requires C, 62.38; H, 5.64.

S-Methyl-3-oxo-5-thienyl-4-pentenethioate(**6e**)

Obtained as a pale yellow solid, 2.03 g (90%), by the reaction of the ketenedithioacetal **5e** in refluxing dioxane for 2 h, exists as the enol form in $CDCl_3$(>95%), m.p. 62°–63°C, IR(KBr); $\nu = 1625$(C=O), 1580, 1500, 1410(C=C), 1265, 1215, 1080 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.30$(s, 3H, SCH_3), 5.50(s, 1H, vinylic, enol), 6.l0(d, J = 16 Hz, 1H, vinylic), 6.92–7.78(m, 4H, arom and vinylic), 12.53(s, 1H, OH) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 10.70$(SCH_3, enol), 11.78(SCH_3, keto), 55.40(CH_2, keto), 100.86(vinylic, enol), 120.02, 123.36, 127.42, 127.80, 128.10, 129.42, 130.88, 132.16, 136.90, 139.08, 140.36(arom and vinylic, keto and enol), 165.64(C-O, enol), 190.07, 191.92(C=O, keto), 194.19(C=O, enol) ppm.

EIMS m/z 226(M^+, 12.6%), 179(47.1%), 137(100%), 123(7.6%). Anal. found C, 52.97; H, 4.39; $C_{10}H_{10}O_2S_2$ requires C, 53.07; H, 4.45.

S-Methyl-2-methyl-3-oxo-5-phenyl-4-pentenethioate(**6f**)

Obtained as a pale yellow solid, 1.57 g (67%), by the reaction of the ketenedithioacetal **5f** in refluxing dioxane for 2 h, exists as the enol form in $CDCl_3$(>95%), m.p. 67°–68°C, IR(KBr); $\nu = 1630$(C=O), 1580, 1550, 1440(C=C) 1260, 1210 cm^{-1}. ^1H NMR(90 MHz, $CDCl_3$) $\delta = 2.10$(s, 3H, CH_3), 2.34(s, 3H, SCH_3), 6.85(d, J = 16 Hz, 1H, vinylic), 7.28–7.72(m, 6H, arom and vinylic), 13.50(s, 1H, OH, enol) ppm. ^{13}C NMR (22.4 MHz, $CDCl_3$) $\delta = 11.51(CH_3)$, 11.78(SCH_3), 105.79 (vinylic), 127.63, 128.79, 128.91, 129.36, 135.80, 138.52, (arom and vinylic), 166.10(C-O, enol), 198.19(C=O) ppm. EIMS m/z 234(M^+, 21.4%), 186(86.8%), 131(100%), 128(8.7%), 115(7.1%). Anal. found C, 66.56; H, 5.95; $C_{13}H_{14}O_2S$ requires C, 65.64; H, 6.02.

S-Methyl-3-oxo-9-phenyl-4,6,8-nonatrienethioate(**8**)

Obtained as a pale yellow solid, 2.5 g (88%), by the reaction of the ketenedithioacetal **7** in refluxing dioxane for 1.5 h, exists as the enol form in $CDCl_3$(>95%), m.p. 108°–110°C, IR(KBr); $\nu = 3400$(OH), 1635(C=O), 1595, 1570, 1550(C=C), 1080, 1000 cm^{-1}. ^1H NMR(300 MHz, $CDCl_3$) $\delta = 2.29$(s, 3H, SCH_3), 5.43(s, 1H, vinylic), 5.74(d, J = 15 Hz, 1H, vinylic), 6.30–6.84(m, 4H, vinylic), 7.10–7.36(m, 6H, arom and vinylic), 12.33 (s, 0.75H, OH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$) $\delta = 10.02$(SCH_3, enol), 11.50(SCH_3, keto), 54.82(CH_2, keto), 100.15(vinylic, enol), 125.72, 127.34, 127.71, 127.98, 134.97, 138.23, 142.36(arom and vinylic), 165.37(C-O, enol), 190.01, 191.57(C=O, keto), 193.54(C=O, enol) ppm. Anal. found C, 70.46; H, 5.83; $C_{10}H_{10}O_2S$ requires C, 70.56; H, 5.92.

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