Synthesis of α-Oxoketene *O*-Alkyl/Aryl, *S*-Alkyl Acetals

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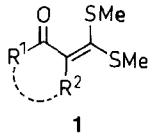
The synthesis of acylketene *O,S*-dialkyl acetals **2a–p** and acylketene *O*-aryl *S*-alkyl acetals **6a–i** is described. The compounds **2a–n** are obtained by base-catalyzed alkylation of the respective β-oxo thiono esters **4a–n** prepared by alkoxythiocarbonylation of active methylene ketones in the presence of sodium *tert*-butoxide. The corresponding *O*-dodecanyl **2o**, *O*-benzyl **2p** and *O*-aryl, *S*-methyl **6a–i** acetals are synthesized via base-catalyzed displacement of the sulfonium salts **5a–b** with the corresponding alkanol or phenol.

The α-oxoketene dithioacetals of the general formula **1** have been proved to be versatile intermediates in organic synthesis.[1] They have also served as precursors for the synthesis of the corresponding *N,S*- and *N,N*-acetals by direct displacement of SMe group(s) with appropriate primary and secondary amines.[1] The displacement of SMe group in **1** is equally facile with carbon nucleophiles, particularly enolate anions, yielding stable 1,4-adducts which are further transformed into novel carbocyclic and heterocyclic compounds.[1,2] Similarly, we have shown in our earlier work, that **1** undergoes displacement with alkoxide ions to give intermediate *O,S*-acetals which react in situ with either guanidine or hydrazine hydrate to afford the corresponding alkoxypyrimidines[3] or alkoxypyrazoles[4] in good yields. However, our attempts to isolate *O,S*-acetals **2** by direct treatment of **1** with sodium alkoxides in alkanol under varying conditions were not successful. Schroth and co-workers,[5] in an isolated example, have reported the synthesis of α-benzoylketene *O,S*-dimethyl acetal (**2a**). The α-benzoylketene dithioacetal was quaternized with dimethyl sulfate to give the corresponding activated sulfonium salt **5a** which underwent smooth displacement with sodium methoxide in methanol to afford a mixture of benzoylketene *O,S*-dimethyl acetal (**2a**) (72%) and the corresponding dithioacetal **1a** (R^1 = Ph, R^2 = H) (13%) by demethylation. Despite extensive work on acylketene dithioacetals[1] and the growing interest in acylketene acetals,[6] the chemistry of the corresponding acylketene *O,S*-acetals has not been investigated and their preparation either directly from the active methylene ketones or through displacement of SMe group by alkoxide ions appears to have received little attention. During the course of our studies on acylketene dithioacetals,[1] we became interested in the chemistry of acylketene *O,S*-acetals and have developed synthetic routes for these new class of intermediates from active methylene ketones. The results of these studies are reported in this paper.



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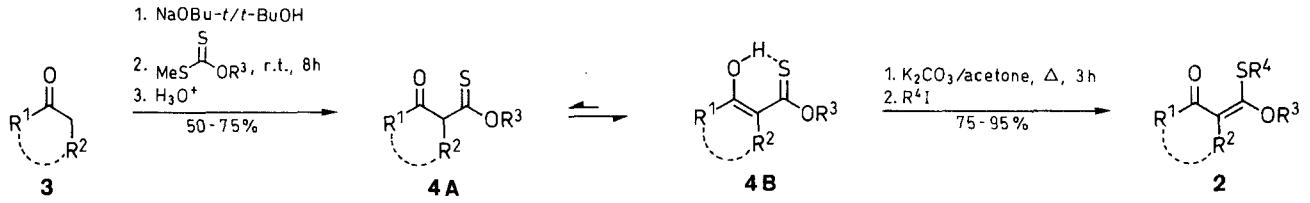
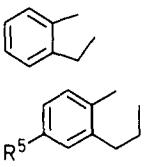
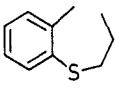
There is no satisfactory general procedure described in the literature for the synthesis of acylketene *O,S*-acetals. In one report, sodium salts of *O*-ethyl benzoyl- and acetyl thioacetates were alkylated with methyl iodide to afford the corresponding *O*-ethyl, *S*-methyl *O,S*-acetals in low yields.[7] Similarly, the tridentate anion from malonic acid monothione ester is reported to yield a mixture of *C*- and *S*-alkylated products under similar alkylation conditions.[8] The β-oxo thiono esters required in these reactions have been prepared in moderate yields either by desulfuration of *O*-ethyl *S*-(acetonyl or phenacyl), dithiocarbonate[7] or via sulfhydrolysis of 3-oxoimidomalonic ester with hydrogen sulfide in pyridine.[8]

Our attempts to develop a one-pot synthesis of α-oxoketene *O,S*-acetals by reacting acetophenone with dimethyl xanthate in the presence of sodium *tert*-butoxide followed by alkylation with methyl iodide, resulted in the formation of a mixture of the corresponding *O,S*-acetal **2a** (65%) and the *S,S*-acetal **1a** (R^1 = Ph, R^2 = H) (15%). The formation of *S,S*-acetal **1a**, though in small quantities, created practical difficulties for separation by column chromatography since both *O,S*- and *S,S*-acetals had the same R_f value. Therefore, the isolation of the corresponding β-oxo thiono esters **4** became necessary which could be separately examined for the alkylation studies. In a separate experiment, acetophenone enolate was reacted with dimethyl dithiocarbonate in the presence of sodium *tert*-butoxide to yield after workup and column chromatography the corresponding β-benzoylthiono ester **4a** in 71% yield.[9] The regioselective *S*-alkylation of **4a** was best achieved by treatment with methyl iodide in the presence of anhydrous potassium carbonate in acetone to afford the corresponding *O,S*-acetal **2a** in 95% yield. Similarly the other thiono esters **4b–h** were obtained in 69–75% overall yields as described above and were subsequently alkylated to afford the corresponding *O,S*-acetals **2b–h** in 85–95% overall yields under the described conditions (Scheme 1). However, attempted preparation of α-acetyl thiono ester by treatment of acetone enolate with *O,S*-dimethyl dithiocarbonate under these conditions resulted in a complex product mixture. Under similar conditions, the thiono ester from cyclohexanone was obtained in moderate yield (50%) which on methylation afforded the cyclic *O,S*-acetal **2i** in 75% yield. Similarly, the thiono esters **4j–n** derived from cyclic ketones **3j–n** were prepared and alkylated to afford the corresponding *O,S*-acetals **2j–n** in 87–93% overall yields. The ^{1}H NMR spectra of **4a–n** revealed that the thiono esters exist in enol form (> 98%).

The present procedure was, however, not successful for the preparation of higher *O*-alkyl, *O*-benzyl and *O*-aryl, *S*-methyl acetals. Attempted reaction of enolates with the respective dithiocarbonates (*S*-methyl, *O*-phenyl dithiocarbonate, *O*-benzyl, *S*-methyl dithiocarbonate) gave mixture of several products. Therefore, these *O,S*-acetals



2–4	R^1	R^2	R^3	R^4
a	Ph	H	Me	Me
b	4-ClC_6H_4	H	Me	Me
c	2-furyl	H	Me	Me
d	2-thienyl	H	Me	Me
e	Ph	H	Et	Et
f	Ph	H	Pr	Me
g	4-$MeOC_6H_4$	H	Pr	Me
h	Ph	H	Bu	Me
i	$-(CH_2)_4-$		Et	Me

2–4	R^1	R^2	R^3	R^4
j			Me	Me
k	$R^5 = H$		Me	Me
l	$R^5 = MeO$		Me	Me
m	$R^5 = H$		Et	Me
n			Me	Me

Scheme 1

Table 1. β-Oxo Thiono Esters **4a–n** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula[a]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)
4a	71	43–44	$C_{10}H_{10}O_2S$ (194.2)	1603, 1578, 1495, 1455, 1403	4.00 (s, 3H, OCH_3), 6.36 (s, 1H, =CH), 7.25–7.50 (m, $3H_{arom}$), 7.63–7.94 (m, $2H_{arom}$), 14.15 (s, 1H, OH, exchangeable with D_2O)
4b	73	86–87	$C_{10}H_9ClO_2S$ (228.7)	1600, 1550, 1485, 1440	4.06 (s, 3H, OCH_3), 6.20 (s, 1H, =CH), 7.30 (d, $2H_{arom}$, $J = 8$), 7.66 (d, $2H_{arom}$, $J = 8$), 13.96 (s, 1H, OH, exchangeable with D_2O)
4c	69	viscous liquid	$C_8H_8O_3S$ (184.2)	1622, 1544, 1470[b]	4.01 (s, 3H, OCH_3), 6.26 (s, 1H, =CH), 6.40–6.56 (m, 1H, H-4′$_{furyl}$), 7.01 (d, 1H, H-3′$_{furyl}$, $J = 3$), 7.49 (d, 1H, H-5′$_{furyl}$, $J = 3$), 13.64 (s, 1H, OH, exchangeable with D_2O)
4d	70	viscous liquid	$C_8H_8O_2S_2$ (200.3)	1595, 1505, 1410[b]	4.03 (s), 4.06 (s, 3H, OCH_3), 6.22 (s, 1H, =CH), 6.93–7.13 (m, 1H, H-4′$_{thienyl}$), 7.26–7.87 (m, 2H, H-3′ & H-5′$_{thienyl}$), 13.97 (s, 1H, OH, exchangeable with D_2O)
4e	71	viscous liquid	viscous liquid[7]	–	–
4f	72	viscous liquid	$C_{12}H_{14}O_2S$ (222.3)	1605, 1572, 1450, 1400[b]	1.03 (t, 3H, CH_3, $J = 7$), 1.80 (sext, 2H, $OCH_2CH_2CH_3$, $J = 7$), 4.40 (q, 2H, $OCH_2CH_2CH_3$, $J = 8$), 6.33 (s, 1H, =CH), 7.20–7.56 (m, $3H_{arom}$), 7.76–8.07 (m, $2H_{arom}$), 14.06 (s, 1H, OH, exchangeable with D_2O)
4g	70	viscous liquid	$C_{13}H_{16}O_3S$ (252.3)	1600, 1568, 1507, 1430[b]	1.03 (t, 3H, CH_3, $J = 7$), 1.80 (sext, 2H, $OCH_2CH_2CH_3$, $J = 7$), 3.79 (s, 3H, OCH_3), 4.36 (t, 2H, $OCH_2CH_2CH_3$, $J = 7$), 6.24 (s, 1H, =CH), 6.85 (d, $2H_{arom}$, $J = 9$), 7.77 (d, $2H_{arom}$, $J = 9$), 14.11 (s, 1H, OH, exchangeable with D_2O)
4h	75	viscous liquid	$C_{13}H_{16}O_2S$ (236.3)	1600, 1500, 1460, 1410[b]	0.96 (t, 3H, CH_3, $J = 7$), 1.23–1.89 [m, 4H, $(CH_2)_2$], 4.41 (t, 2H, OCH_2, $J = 7$), 6.38 (s, 1H, =CH), 7.30–7.56 (m, $3H_{arom}$), 7.7–8.0 (m, $2H_{arom}$), 14.10 (s, 1H, OH, exchangeable with D_2O)
4i	50	viscous liquid	$C_9H_{14}O_2S$ (186.3)	1650, 1500, 1470, 1460	1.41 (t, 3H, OCH_2CH_3, $J = 7$), 1.43–1.82 [br s, 4H, $(CH_2)_2$], 2.13–2.60 [br s, 4H, $(CH)_2$], 4.45 (q, 2H, OCH_2CH_3, $J = 7$), 14.35 (s, 1H, OH, exchangeable with D_2O)
4j	61	96–97	$C_{11}H_{10}O_2S$ (206.3)	1615, 1532, 1470, 1458	3.58 (s, 2H, CH_2), 4.11 (s, 3H, OCH_3), 7.21–7.45 (m, $3H_{arom}$), 7.59–7.82 (m, $1H_{arom}$), 12.86 (s, 1H, OH, exchangeable with D_2O)
4k	71	56–57	$C_{12}H_{12}O_2S$ (220.3)	1605, 1587, 1545, 1445	2.71 [s, 4H, $(CH_2)_2$], 4.05 (s, 3H, OCH_3), 7.00–7.36 (m, $3H_{arom}$), 7.86–8.03 (m, $1H_{arom}$), 14.30 (s, 1H, OH, exchangeable with D_2O)
4l	68	74–75	$C_{13}H_{14}O_3S$ (250.3)	1628, 1593, 1507, 1403	2.70 [s, 4H, $(CH_2)_2$], 3.80 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3), 6.63–6.90 (m, $2H_{arom}$), 7.88 (d, $1H_{arom}$, $J = 8$), 14.53 (s, 1H, OH, exchangeable with D_2O)
4m	69	69–70	$C_{13}H_{14}O_2S$ (234.3)	1608, 1590, 1548, 1450, 1420	1.36 (t, 3H, OCH_2CH_3, $J = 7$), 2.70 [s, 4H, $(CH_2)_2$], 4.46 (q, 2H, OCH_2CH_3, $J = 7$), 7.03–7.41 (m, $3H_{arom}$), 7.83–8.01 (m, $1H_{arom}$), 14.50 (s, 1H, OH, exchangeable with D_2O)
4n	71	81–82	$C_{12}H_{12}O_2S_2$ (252.3)	1592, 1570, 1545, 1407	2.53 (t, 2H, CH_2, $J = 6$), 3.30 (t, 2H, SCH_2, $J = 6$), 4.10 (s, 3H, OCH_3), 7.23–7.76 (m, $4H_{arom}$), 14.38 (s, 1H, OH, exchangeable with D_2O)

[a] Satisfactory microanalyses obtained: C ± 0.29, H ± 0.27. [b] In $CHCl_3$.

Table 2. α-Acylketene *O,S*-Dialkyl Acetals **2a–p** Prepared

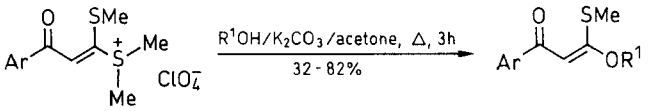
Product	Yield (%)	mp (°C)	Molecular Formula[a]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	MS (70 eV) m/z (M^+, %)
2a	95	67–68	$C_{11}H_{12}O_2S$ (208.3)	1635, 1611, 1592, 1570	2.28 (s, 3H, SCH_3), 3.98 (s, 3H, OCH_3), 6.38 (s, 1H, =CH), 7.31–7.52 (m, $3H_{arom}$), 7.80–8.03 (m, $2H_{arom}$)	208 (27)
2b	93	131–132	$C_{11}H_{11}ClO_2S$ (242.7)	1622, 1590, 1569, 1440	2.28 (s, 3H, SCH_3), 3.94 (s, 3H, OCH_3), 6.33 (s, 1H, =CH), 7.36 (d, $2H_{arom}$), 7.36 (d, $2H_{arom}$, J = 8), 7.82 (d, $2H_{arom}$, J = 8)	242 (19)
2c	88	69–70	$C_9H_{10}O_3S$ (198.2)	1613, 1571, 1510, 1430	2.30 (s, 3H, SCH_3), 3.93 (s, 3H, OCH_3), 6.28 (s, 1H, =CH), 6.41–6.57 (m, 1H, H-4′$_{furyl}$), 7.41 (d, 1H, H-3′$_{furyl}$, J = 3), 7.51 (br s, 1H, H-5′$_{furyl}$)	198 (56)
2d	88	56–57	$C_9H_{10}O_2S_2$ (214.3)	1603, 1517, 1432, 1415	2.27 (s, 3H, SCH_3), 3.94 (s, 3H, OCH_3), 6.28 (s, 1H, =CH), 6.98–7.18 (m, $1H_{thienyl}$), 7.48–7.80 (m, $2H_{thienyl}$)	
2e	95	46–47	$C_{13}H_{16}O_2S$ (236.3)	1625, 1595, 1572, 1468	1.05–1.53 (m, 6H, $SCH_2\underline{CH_3}$ and $OCH_2\underline{CH_3}$), 2.80 (q, 2H, $SC\underline{H_2}CH_3$, J = 7), 4.08 (q, 2H, $OC\underline{H_2}CH_3$, J = 7), 6.33 (s, 1H, =CH), 7.20–7.48 (m, $3H_{arom}$), 7.76–7.98 (m, $2H_{arom}$)	236 (18)
2f	89	89–90	$C_{13}H_{16}O_2S$ (236.3)	1623, 1573, 1515	1.03 (t, 3H, $OCH_2CH_2C\underline{H_3}$, J = 6), 1.83 (sext, 2H, $OCH_2C\underline{H_2}CH_3$, J = 6), 2.30 (s, 3H, SCH_3), 4.06 (t, 2H, $OC\underline{H_2}CH_2CH_3$, J = 6), 6.40 (s, 1H, =CH), 7.28–7.63 (m, $3H_{arom}$), 7.87–8.10 (m, $2H_{arom}$)	236 (15)
2g	89	77–78	$C_{14}H_{18}O_3S$ (266.3)	1620, 1600, 1570	1.03 (t, 3H, $OCH_2CH_2C\underline{H_3}$, J = 6), 1.87 (sext, 2H $OCH_2C\underline{H_2}CH_3$, J = 6), 2.30 (s, 3H, SCH_3), 3.83 (s, 3H, OCH_3), 4.05 (t, 2H, $OC\underline{H_2}CH_2CH_3$, J = 6), 6.38 (s, 1H, =CH), 6.94 (d, $2H_{arom}$, J = 8), 7.94 (d, $2H_{arom}$, J = 8)	266 (10)
2h	85	51–52	$C_{14}H_{18}O_2S$ (250.3)	1640, 1591, 1520	0.98 [t, 3H, $C\underline{H_3}(CH_2)_2CH_2O$, J = 6], 1.24–1.92 [m, 4H, $OCH_2(C\underline{H_2})_2CH_3$], 2.30 (s, 3H, SCH_3), 4.07 (t, 2H, OCH_2, J = 6), 6.50 (s, 1H, =CH), 7.31–7.72 (m, $3H_{arom}$), 7.9–8.21 (m, $2H_{arom}$)	250 (17)
2i	75	viscous liquid	$C_{10}H_{16}O_2S$ (200.3)	1665, 1590	1.32 (t, 3H, CH_3, J = 7), 1.51–2.08 [m, 4H, $(CH_2)_2$], 2.28 (s, 3H, SCH_3), 2.08–2.78 [m, 4H, $(CH_2)_2$], 3.92 (q, 2H, OCH_2CH_3, J = 7)	
2j	87	48–49	$C_{12}H_{12}O_2S$ (220.3)	1652, 1610, 1529, 1428	2.30 (s, 3H, SCH_3), 3.61 (s, 2H, CH_2), 3.97 (s, 3H, OCH_3), 7.25–7.60 (m, $3H_{arom}$), 7.73–7.98 (m, $1H_{arom}$)	220 (5)
2k	88	65–66	$C_{13}H_{14}O_2S$ (234.3)	1605, 1551, 1498	2.27 (s, 3H, SCH_3), 2.88 [s, 4H, $(C\underline{H_2})_2CH_2$], 3.94 (s, 3H, OCH_3), 7.10–7.50 (m, $3H_{arom}$), 8.00–8.18 (m, $1H_{arom}$)	234 (45)
2l	89	82–83	$C_{14}H_{16}O_3S$ (264.3)	1645, 1610, 1580, 1525	2.27 (s, 3H, SCH_3), 2.87 [s, 4H, $(CH_2)_2$], 3.93 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.60–6.93 (m, $2H_{arom}$), 8.05 (d, $1H_{arom}$, J = 9)	–
2m	91	viscous liquid	$C_{14}H_{16}O_2S$ (248.3)	1742, 1650, 1604[b]	1.37 (t, 3H, $OCH_2C\underline{H_3}$, J = 7), 2.28 (s, 3H, SCH_3), 2.86 [s, 4H, $(CH_2)_2$], 3.95 (q, $OC\underline{H_2}CH_3$, J = 7), 7.07–7.48 (m, $3H_{arom}$), 8.01–8.20 (m, $1H_{arom}$)	248 (3)
2n	93	88–89	$C_{13}H_{14}O_2S_2$ (266.4)	1622, 1589, 1500	2.27 (s, 3H, SCH_3), 2.63 (t, 2H, CH_2, J = 6), 3.03 (t, 2H, CH_2, J = 6), 3.98 (s, 3H, OCH_3), 7.22–7.45 (m, $3H_{arom}$), 7.56–7.76 (m, $1H_{arom}$)	266 (83)
2o	32	38–39	$C_{22}H_{34}O_2S$ (362.6)	1640, 1600, 1500, 1465	0.98 (br t, 3H, CH_3), 1.10–1.6 [br s, 20H, $(CH_2)_{10}$], 2.29 (s, 3H, SCH_3), 4.02 (t, 2H, OCH_2), 6.5 (s, 1H, =CH), 7.35–7.62 (m, $3H_{arom}$), 7.87–8.1 (m, $2H_{arom}$)	
2p	68	101–102	$C_{17}H_{16}O_2S$ (284.4)	1629, 1500, 1375, 1258, 1171	2.27 (s, 3H, SCH_3), 5.11 (s, 2H, CH_2), 6.50 (s, 1H, =CH), 7.40 (s, $8H_{arom}$), 7.73–7.90 (m, $2H_{arom}$)	224 (27)

[a] Satisfactory microanalysis obtained: C ± 0.28, H ± 0.27.

[b] In CCl_4.

could only be prepared by displacement reaction on the corresponding dimethylsulfonium salts derived from the respective dithioacetals[5] (Scheme 2). Thus the dimethylsulfonium perchlorate **5a** on reaction with phenol in the presence of anhydrous potassium carbonate in acetone afforded the corresponding *O*-phenyl, *S*-methyl acetal **6a** in 68% yield. Similarly, the other substituted *O*-aryl-*S*-methyl acetals **6b–h** were prepared from **5a–b** and substituted phenols in 70–82% overall yields. The cyclic *O*-phenyl acetal **6i** from tetralone could be prepared from the sulfonium salt **5c** in 69% yield under identical conditions (Scheme 3). Similarly, displacement by dodecanol and benzyl alcohol on **5a** yielded **2o** and **2p** in 32% and 68% yields, respectively. The oxoketene dithioacetals from cyclohexanone and acetone failed to give the corresponding sulfonium salts under the reported conditions.[5] Therefore, the related *O*-aryl, *S*-methylacetals could not be prepared by this methodology. Further work to study the reactivity of these new intermediates towards various nucleophiles is in progress.

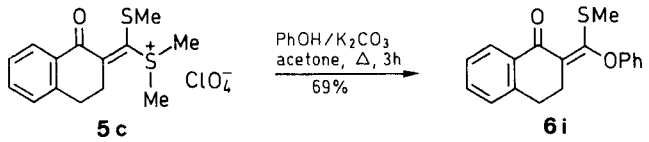
The α-oxoketene *O,S*-acetals might in principle exist either as *E*- or *Z*-geometrical isomer or as a mixture of both. In all cases, only one stereoisomer was obtained which was evident from their sharp melting points and also from their ^1H NMR spectra which exhibited single sharp signals for vinylic, SCH_3, and OCH_3 (or *O*-alkyl) groups. All the acyclic *O,S*-acetals **2a–h** exhibited signals due to vinylic proton between δ = 6.28–6.50, SCH_3 between δ = 2.27–2.30 (SCH_2 in **2e** at δ = 2.80), OCH_3 (or OCH_2) between δ = 3.92–4.08. The cyclic *O,S*-acetals **2i–n** also displayed signals due to SCH_3 and OCH_3 (OCH_2) protons at δ = 2.27–2.29 and δ = 3.92–4.02, respectively. The stereochemistry of these compounds was established on the basis of difference ^1H NMR NOE experiments carried out on *O,S*-acetals



5 2, 6

5	2, 6	Ar	R^1
5a	2o	Ph	$C_{12}H_{25}$
5a	2p	Ph	$PhCH_2$
5a	6a	Ph	Ph
5a	6b	2-thienyl	Ph
5a	6c	4-$MeOC_6H_4$	1-naphthyl
5a	6d	Ph	2-ClC_6H_4
5a	6e	Ph	3-MeC_6H_4
5b	6f	4-$MeOC_6H_4$	4-ClC_6H_4
5a	6g	Ph	4-AcC_6H_4
5a	6h	Ph	2-$MeO_2CC_6H_4$

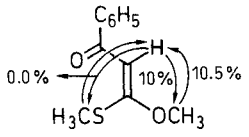
Scheme 2



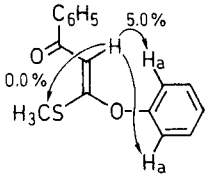
5c 6i

Scheme 3

2a and **6a**. Thus the irradiation of vinylic proton (δ = 6.38) in **2a** gave NOE on OCH_3 (δ = 3.98) only, which was further confirmed by reverse experiment by irradiating OCH_3 signal when the NOE enhancement of vinylic proton was observed. The assignment was further confirmed by 2D NOESY spectra of **2a** which showed a cross peak between vinylic CH and OCH_3 group while no cross peak was observed between SCH_3 and vinylic proton. Similarly, in the case of *O*-phenyl acetal **6a**, irradiation of vinylic CH signal (δ = 6.3) gave NOE enhancement on aryl protons while irradiation of SCH_3 (δ = 2.37) showed no NOE enhancement on vinylic proton. These observations support *Z*-stereochemistry for both *O*-alkyl and *O*-phenyl *O,S*-acetals. The cyclic *O,S*-acetals (**2i–n**) were also assigned *Z*-stereochemistry, since chemical shift values for SCH_3 signal (*cis* to CO) were found to be very similar to those of acyclic ones.



2a



6a

Melting points were determined on a Thomas Hoover (Capillary method) apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer and ^1H NMR spectra on a Varian EM-390 90 MHz spectrometer. 2D-NOESY spectra (mixing time, 1 sec) and difference NOE ^1H NMR experiments were performed on AMX 400 NMR spectrometer. Mass spectra were obtained on Jeol JMS-D-300 instruments. Microanalyses were performed on Hearaus automatic analyser.

The starting dialkyl dithiocarbonates,[10] dimethylsulfonium perchlorates[5] **5a–c** were prepared according to the reported procedures.

β-Oxo Thiono Esters 4a–n; General Procedure:
To an ice-cold stirring suspension of sodium *tert*-butoxide (38.4 g, 0.4 mol, prepared from 9.2 g, 0.4 atom of sodium) in *tert*-butyl alcohol (150 mL) were added dropwise sequentially dialkyl dithiocarbonate (0.2 mol) and the respective ketone (0.2 mol), and the

Table 3. Acyl Ketene *O*-Aryl *S*-Methyl Acetals **6a–i** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula[a]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	MS (70 eV) *m/z* (%)
6a	68	66–67	$C_{16}H_{14}O_2S$ (270.34)	1622, 1495, 1475, 1240, 1190	2.37 (s, 3H, SCH_3), 6.30 (s, 1H, =CH), 7.05–7.56 (m, $8H_{arom}$), 7.57–7.73 (m, $2H_{arom}$)	223 (M^+-47, 100)
6b	76	104–105	$C_{14}H_{12}O_2S_2$ (276.4)	1605, 1518, 1480, 1410, 1240	2.41 (s, 3H, SCH_3), 6.17 (s, 1H, =CH), 7.01 (br t, $1H_{thienyl}$, J = 5 Hz), 7.18–7.65 (m, $7H_{arom+thienyl}$)	276 (M^+, 1), 229 (M^+-47, 100)
6c	70	62–63	$C_{21}H_{18}O_3S$ (350.4)	1655, 1618, 1518, 1259, 1162	2.52 (s, 3H, SCH_3), 3.81 (s, 3H, OCH_3), 6.52 (s, 1H, =CH), 6.92 (d, $2H_{arom}$, J = 9), 7.42–8.18 (m, $9H_{arom}$)	350 (M^+, 1), 303 (M^+-47, 40)
6d	72	82–83	$C_{16}H_{13}ClO_2S$ (304.8)	1658, 1530, 1485, 1265, 1225	2.41 (s, 3H, SCH_3), 6.19 (s, 1H, =CH), 7.09–7.58 (m, $7H_{arom}$), 7.59–7.77 (m, $2H_{arom}$)	304 (M^+, 1), 257 (M^+-47, 100), 259 (35)
6e	73	71–72	$C_{17}H_{16}O_2S$ (284.4)	1630, 1500, 1250, 1230, 1165	2.39 (s, 3H, SCH_3), 2.47 (s, 3H, CH_3), 6.29 (s, 1H, =CH), 6.80–7.61 (m, $7H_{arom}$), 7.61–7.88 (m, $2H_{arom}$)	237 (M^+-47, 96)
6f	72	73–74	$C_{17}H_{15}ClO_3S$ (334.8)	1625, 1600, 1506, 1472, 1250, 1208	2.40 (s, 3H, SCH_3), 3.79 (s, 3H, OCH_3), 6.30 (s, 1H, =CH), 6.85 (d, $2H_{arom}$, J = 9), 7.10 (d, $2H_{arom}$, J = 9), 7.39 (d, $2H_{arom}$, J = 9), 7.68 (d, $2H_{arom}$, J = 9)	287 (M^+-47, 98), 289 (33)
6g	71	111–112	$C_{18}H_{16}O_3S$ (312.4)	1680, 1625, 1590, 1495, 1245, 1210	2.41 (s, 3H, $COCH_3$), 2.63 (s, 3H, SCH_3), 6.48 (s, 1H, =CH), 7.17–7.44 (m, $5H_{arom}$), 7.63–7.80 (m, $2H_{arom}$), 7.92–8.12 (m, $2H_{arom}$)	–
6h	82	117–118	$C_{18}H_{16}O_4S$ (328.4)	1720, 1615, 1600, 1498, 1275	2.55 (s, 3H, SCH_3), 3.88 (s, 3H, OCH_3), 6.09 (s, 1H, =CH), 7.23–7.53 (m, $5H_{arom}$), 7.56–7.85 (m, $3H_{arom}$), 7.93–8.20 (m, $2H_{arom}$)	281 (M^+-47, 73), 238 (62)
6i	69	125–126	$C_{18}H_{16}O_2S$ (296.4)	1597, 1632, 1510, 1488, 1320, 1210	2.40 (s, 3H, SCH_3), 2.75 [br s, 4H, $(CH_2)_2$], 6.97–7.43 (m, $8H_{arom}$), 8.03–8.17 (m, $1H_{arom}$)	249 (M^+-47, 100)

[a] Satisfactory microanalyses obtained: C ± 0.30, H ± 0.25.

resulting mixture was stirred at r.t. for 8–10 h. It was then poured into crushed ice, acidified with 50% HCl (50 mL), extracted with benzene (3 × 100 mL) and the combined extracts were washed with water (3 × 150 mL), dried (Na_2SO_4) and concentrated to give the crude thiono esters, which were purified by column chromatography over silica gel using hexane as eluent (Table 1).

Acyl Ketene *O,S*-dialkyl Acetals 2a–n; General Procedure:
A suspension of β-oxo thiono ester **3** (0.2 mol) and anhydr. K_2CO_3 (83 g, 0.6 mol), in dry acetone (150 mL) was refluxed with stirring for 3 h and then cooled to r.t. Appropriate alkyl halide (0.4 mol) was added dropwise with cooling (0–5 °C) and stirring and the resulting mixture was further stirred at r.t. temperature for 10 h. K_2CO_3 was filtered, washed with acetone (75 mL) and the combined filtrate was concentrated on a water bath. The residue was then poured into crushed ice, extracted with $CHCl_3$ (2 × 100 mL), the combined extracts were washed with water (3 × 100 mL), dried (Na_2SO_4) and evaporated to give the *O,S*-acetals, which were further purified by column chromatography over silica gel using EtOAc/hexane (1:99) as eluent (Table 2).

Acyl Ketene *O*-Alkyl/Aryl, *S*-methyl Acetals 2o–p, 6a–i; General Procedure:
A suspension of the appropriate alcohol or phenol (30 mmol) and anhydr. K_2CO_3 (12.50 g, 90 mmol) in anhydr. acetone (100 mL) was refluxed with stirring for 2–3 h. The resulting mixture was cooled to 0–5 °C and the dimethylsulfonium perchlorate salt **5a–b** (10 mmol) was added in small portions with stirring. The mixture was further stirred for 8 h, filtered, washed with acetone (75 mL) and the filtrate concentrated on water bath. The residue was poured into crushed ice, extracted with $CHCl_3$ (2 × 100 mL), washed with 10% NaOH solution (2 × 50 mL) (for **6a–i**) and then with water (3 × 100 mL), dried Na_2SO_4 and evaporated to give crude products, which were further purified by column chromatography over silica gel using EtOAc/hexane (1:99) as eluent (Table 3).

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