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A Convenient Synthesis of Some α-Oxoketene-*N,S*- and *N,N*-Acetals

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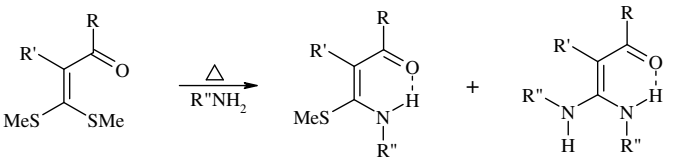
Some α-oxoketene-*N,S*- and *N,N*-acetals were selectively synthesized in good to excellent yields by the reaction of 1,1-dimethoxy-4,4-di(methylthio)-3-buten-2-one with primary and secondary amines under moderate conditions. Secondary amines in reaction with α-oxoketene dithioacetal yielded double-substitution products exclusively, whereas primary amines under the same conditions yielded the mono-substituted products as exclusive or main products.

Keywords: Nucleophilic addition-elimination, α-Oxoketene dithioacetals, α-Oxoketene-*N, S*-acetals, α-Oxoketene-*N,N*-acetals, Double-substitution

INTRODUCTION

α-Oxoketene-*N,S*- and *N,N*-acetals **II** and **III** have been used as versatile three-carbon synthons for the synthesis of various heterocyclic compounds [1-10]. These types of intermediates are generally prepared by nucleophilic addition-elimination reactions of α-oxoketene dithioacetals **I** with amines in boiling solvents such as absolute ethanol [11], a mixture of xylene and DMF [12,13], and ethanoic acid or propanoic acid [14]. Likewise, aromatic amine derivatives are prepared by heating dithioacetals **I** with the appropriate aromatic amine at 150-160 ºC in the absence of solvent [11] or by conversion of the amine into its *N*-anion by reaction with *n*-BuLi in THF at -78 ºC [15]. In these reactions, generally a mixture of α-oxoketene-*N,S*- and *N,N*-acetals **II** and **III** are obtained (Scheme 1). This gives rise to a low yield of the desired product and uses severe work up procedures.

Due to the importance of these synthons in synthesizing complicated compounds [1], presenting a facile and selective method to synthesize these intermediates and improve the total yields of the target molecules would be very advantageous. Herein, we wish to report a more convenient and selective method to prepare a newly developed, practical version of these synthons [15,16] under moderate conditions from α-oxoketene dithioacetal **1**.



I **II** **III**

R, R': H, alkyl, cycloalkyl, aryl
R" : alkyl, cycloalkyl, aryl

Scheme 1

EXPERIMENTAL

All starting materials were purchased from Aldrich and Merck and used without further purification. Melting points were determined using a Stuart Scientific SMP2 apparatus and

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are uncorrected. IR spectra were recorded on Shimadzu IR-435 spectrometer. ^{1}H NMR spectra were recorded using a Bruker DRX AVANCE 500 MHz spectrometer using $CDCl_3$ as a solvent. ^{13}C NMR spectra were obtained with a Bruker 125 MHz NMR AC80 spectrometer. Mass spectra were recorded on a Platform II Micromass apparatus. The elemental analysis of all new compounds was performed on a Heraeus CHN-O-RAPID elemental analyzer. Column chromatography was performed using silica gel (Merck No. 60) and TLC analysis was carried out on silica plates (Merck) using a mixture of petroleum ether/ethyl acetate (1:1) as an eluent.

α-Oxoketene-*N,S*- and *N,N*-acetals 2, 3: General Procedure

To a solution of the dithioacetal **1** (16) (666 m, 3 mmol) in CH_3CN (10 ml), the appropriate amine was added and the mixture was stirred at room temperature for the length of time as shown in Table 1. The solvent was evaporated to afford an oily viscous crude product, which was purified by flash column chromatography. In the case of ketene-*N,S*-acetals **2e** and **2f** the reaction mixture was refluxed for 6 h.

Spectral Data

1,1-Dimethoxy-4-methylamino-4-methylthio-3-buten-2-one (2a). Yellow solid (additional purification was not necessary) m.p.: 59-61 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H, SCH_3), 3.02 (d, 3H, NCH_3, *J* = 5.0 Hz), 3.42 (s, 6H, 2 OCH_3), 4.58 (s, 1H, [C**H**$(OMe)_2$], 5.37 (s, 1H, =CH), 11.42 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (SCH_3), 30.1 (NCH_3), 53.7 ($2OCH_3$), 85.2 (=CH), 103.7 [$CH(OMe)_2$], 171.9 (C=CH), 186.5 (C=O); IR (KBr, cm^{-1}) υ 2936, 1584, 1482, 1286, 1106, 728; MS (EI, 70 eV) *m/z* (%) 205 (M^+, 53), 175 (M^+-CH_2O, 75), 158 (M^+-CH_3S, 21), 130 [M^+-$CH(OMe)_2$], 100), 75 $CH(OMe)_2$, 89); Anal. Calcd. for $C_8H_{15}NO_3S$: C, 46.83; H, 7.32; N, 6.83%. Found: C, 46.9; H, 7.3; N, 6.8%.

1,1-Dimethoxy-4-ethylamino-4-methylthio-3-buten-2-one (2b). Brown viscous liquid (additional purification was not necessary); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, *J* = 7.2 Hz 3H, C**H**$_3$$CH_2$), 2.28 (s, 3H, SCH_3), 3.22-3.29 (m, 8H, CH_3C**H**$_2$NH+ $2OCH_3$), 4.43 (s, 1H, C**H**$(OMe)_2$, 5.22 (s, 1H, =CH), 11.33 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (SCH_3), 14.5 (**C**H_3CH_2), 38.7 (CH_2N), 53.9 ($2OCH_3$), 85.1 (=CH), 103.8 [**C**$H(OMe)_2$], 170.6 (**C**=CH), 186.5 (C=O); IR (Neat, cm^{-1}) υ 2946, 1589, 1480, 1284, 738; MS (EI, 70 eV) *m/z* (%) 219 (M^+, 3), 144 [M^+-$CH(OMe)_2$], 55), 75 $CH(OMe)_2$, 100); Anal. Calcd. for $C_9H_{17}NO_3S$: C, 49.32; H, 7.76; N, 6.39%. Found: C, 49.3; H, 7.7; N, 6.4%.

1,1-Dimethoxy-4-buthylamino-4-methylthio-3-buten-2-one (2c). Brown viscous liquid (additional purification was not necessary); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.25 Hz, 3H, C**H**$_3$$(CH_2)_3$), 1.34 (hx, *J* = 7.25 Hz, 2H, CH_3C**H**$_2$$(CH_2)_2$), 1.54 (quin, *J* = 7.25 Hz, 2H, CH_3CH_2C**H**$_2$$CH_2$), 2.32 (s, 3H, SCH_3), 3.21-3.34 (m, 8H, C**H**$_2$NH, and $2OCH_3$), 4.49 (s, 1H, $CH(OMe)_2$), 5.27 (s, 1H, =CH), 11.49 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.1 (SCH_3), 19.9 (CH_2), 31.2 (CH_2), 43.7 (CH_2NH), 53.9 ($2OCH_3$), 85.1 (=CH), 103.9 ($CH(OMe)_2$), 170.8 (C=CH), 186.4 (C=O); IR (Neat, cm^{-1}) υ 2976, 1585, 1479, 1276, 1106, 741; MS (EI, 70 eV) *m/z* (%) 247 (M^+, 2), 172 (M^+-$CH(OMe)_2$, 13), 75 $CH(OMe)_2$, 71); Anal. Calcd. for $C_{11}H_{21}NO_3S$: C, 53.44; H, 8.50; N, 5.67%. Found: C, 53.1; H, 8.4; N, 5.6%.

1,1-Dimethoxy-4-benzylamino-4-methylthio-3-buten-2-one (2d). Brown viscous liquid (additional purification was not necessary); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H, SCH_3), 3.35 (s, 6H, $2OCH_3$), 4.48 (d, 2H, CH_2, *J* = 5.7 Hz), 4.54 (s, 1H, C**H**$(OMe)_2$), 5.39 (s, 1H, =CH), 7.21-7.27 (m, 5H, aryl-H), 11.84 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (SCH_3), 47.7 (CH_2), 53.9 ($2OCH_3$), 85.9 (=CH), 103.7 ($CH(OMe)_2$, 127.1, 127.5, 128.6, 136.6 (aryl-C), 170.8 (C=CH), 187.0 (C=O); IR (Neat, cm^{-1}) υ 3162, 1587, 1485, 1219, 1112, 738; MS (EI, 70 eV) *m/z* (%) 281 (M^+, 7), 251 (M^+-CH_2O, 12), 206 (M^+-$CH(OMe)_2$, 100), 91 ($C_6H_5CH_2$, 99), 75 $CH(OMe)_2$, 98); Anal. Calcd. for $C_{14}H_{19}NO_3S$: C, 59.79; H, 6.76; N, 4.98%. Found: C, 60.1; H, 6.9; N, 4.8%.

1,1-Dimethoxy-4-phenylamino-4-methylthio)-3-buten-2-one (2e). Yellow crystalline solid, m.p.: 63-65 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H, SCH_3), 3,44 (s, 6H, $2OCH_3$), 4.64 (s, 1H, C**H**$(OMe)_2$, 5.59 (s, 1H, =CH), 7.22-7.36 (m, 5H, aryl-H), 13.05 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9 (SCH_3), 54.4 ($2OCH_3$), 87.7 (=CH), 104.1 2**C**H$(OMe)_2$, 125.6, 127.0, 129.3, 138.1 (aryl-C), 169.6 (C=CH), 188.3 (C=O); IR (KBr, cm^{-1}) υ 2996, 2936, 1581, 1469, 1248, 1101, 725; MS (EI, 70 eV) *m/z* (%) 267 (M^+, 3), 220 (M^+-SCH_3, 2), 192 [M^+-$CH(OMe)_2$], 28), 77 (C_6H_5, 81), 75 $CH(OMe)_2$, 100); Anal. Calcd. for $C_{13}H1_7O_3NS$: C, 58.43;

H, 6.36; N, 5.24%. Found: C, 59.1; H, 6.4; N, 5.3%.

1,1-Dimethoxy-4-methylthio-4-(p-tolyl)amino-3-buten-2-one (2f). Red-brown solid, m.p.: 58-60 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 3H, SCH_3), 2.27 (s, 3H, 4-$CH_3C_6H_4$), 3.36 (s, 6H, $2OCH_3$), 4.56 (s, 1H, $CH(OMe)_2$, 5.50 (s, 1H, =CH), 7.06 (m, 4H, aryl-H), 12.91 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5 (SCH_3), 20.9 (4-$CH_3C_6H_4$), 54.1 (2 OCH_3), 87.2 (=CH), 103.9 $CH(OMe)_2$, 125.3, 129.6, 135.2, 136.6 (aryl-C), 169.5 (C=CH), 187.8 (C=O); IR (KBr, cm^{-1}) υ 3135, 2921, 1592, 1466, 1294, 1098, 803, 720; MS (EI, 70 eV) *m/z* (%) 281 (M^+, 6), 233 (M^+-SCH_3, 15), 206 [M^+-$CH(OMe)_2$], 64), 91 (4-$CH_3C_6H_4$, 55), 75 $CH(OMe)_2$, 100); Anal. Calcd. for $C_{14}H_{19}O_3NS$: C, 59.79; H, 6.76; N, 4.98%. Found: C, 59.3; H, 6.5; N, 5.0%.

1,1-Dimethoxy-4,4-di(methylamino)-3-buten-2-one (3a). Red-brown solid, m.p.: 137-138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.60 (d, *J* = 3.8 Hz, 6H, $2NCH_3$,), 3.12 (s, 6H, $2OCH_3$), 4.27 (s, 1H, C**H**$(OMe)_2$), 4.70 (s, 1H, =CH), 5.92 (s, 1H, N$\mathbf{H}_E$), 10.32 (s, 1H, N**H**z); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.8 (NCH_3), 28.8 (NCH_3), 53.5 ($2OCH_3$), 75.3 (=CH), 104.1 $CH(OMe)_2$, 163.1 (**C**=CH), 182.6 (C=O); IR (KBr, cm^{-1}) υ 3205, 2936, 1597, 1552, 1454, 1262, 1053, 728; MS (EI, 70 eV) *m/z* (%) 188 (M^+, 21), 158 (M^+-CH_2O, 66), 113 [M^+-$CH(OMe)_2$], 100); 98 [M^+-$CH(OMe)_2$-CH_3], 81); Anal. Calcd. for $C_8H1_6N_2O_3$: C, 50.06; H, 8.51; N, 14.89%. Found: C, 49.5; H, 8.1; N, 14.3%.

3,3-Dimethoxy-1-(imidazolidin-2-ylidene)propan-2-one (3g). Colorless crystalline solid, m.p.: 131-133 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (s, 6H, $2OCH_3$), 3.59 (s, 4H, C$\mathbf{H}_2$C$\mathbf{H}_2$), 4.48 (s, 1H, C**H**$(OMe)_2$), 5.04 (s, 1H, =CH), 6.5-9.5 (br, 2H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.0 (CH_2CH_2), 53.5 ($2OCH_3$), 74.4 (=CH), 103.7 $CH(OMe)_2$, 165.9 (**C**=CH), 185.4 (C=O); IR (KBr, cm^{-1}) υ 3302, 3130, 2958, 1608, 1587, 1326, 1189, 1061, 749; MS (EI, 70 eV) *m/z* (%) 186 (M^+, 19), 156 (M^+-CH_2O, 83), 127 (M^+-$C_2H_5N_2$, 87), 111 [M^+-$CH(OMe)_2$], 100), 75 $CH(OMe)_2$, 87); Anal. Calcd. for $C_8H_{14}N_2O_3$: C, 51.61; H, 7.53; N, 15.05%. Found: C, 51.5; H, 7.4; N, 15.1%.

3,3-Dimethoxy-1-(tetrahydropyrimidin-2-ylidene) propan-2-one (3h). Colorless crystalline solid, m.p.: 158-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (quin, *J* = 5.5 Hz, 2H, $CH_2C\mathbf{H}_2CH_2$,), 3.18-3.26 (m, 10H, $2OCH_3$ and $2CH_2$), 4.43 (s, 1H, C**H**$(OMe)_2$), 4.76 (br, 1H, =CH), 8.0-9.5 (br, 2H, 2NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.9 (CH_2), 38.1 (CH_2), 53.6 ($2OCH_3$), 77.1 (=CH), 103.6 C**H**$(OMe)_2$, 159.6 (**C**=CH), 185.6 (C=O); IR (KBr, cm^{-1}) υ 3135, 2931, 1592, 1482, 1367, 1232, 1053, 808, 736; MS (EI, 70 eV) *m/z* (%) 200 (M^+, 3), 170 (M^+-CH_2O, 6) 125 [M^+-$CH(OMe)_2$], 100); Anal. Calcd. for $C_9H_{16}N_2O_3$: C, 54.00; H, 8.00; N, 14.00%. Found: C, 53.8; H, 7.9; N, 14.1%.

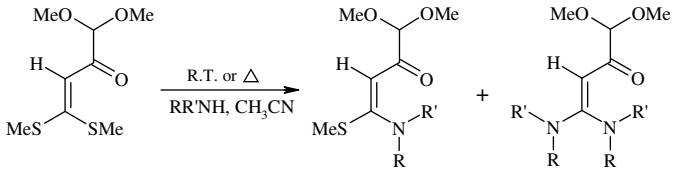
1,1-Dimethoxy-4,4-bis(dimethylamino)-3-buten-2-one (3i). Brown viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.67 (s, 12H, $4NCH_3$), 3.17 (s, 6H, $2OCH_3$), 4.27 (s, 1H, C**H**$(OMe)_2$, 4.55 (s, 1H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.7 (4 NCH_3), 53.5 ($2OCH_3$), 81.4 (=CH), 104.7 **C**$H(OMe)_2$, 168.1 (**C**=CH), 184.5 (C=O); IR (Neat, cm^{-1}) υ 2936, 1665, 1600, 1549, 1482, 1200, 1058, 744; MS (EI, 70 eV) *m/z* (%) 216 (M^+, 3), 143 [M^+-$CH(OMe)_2$], 100), 98 [M^+-$CH(OMe)_2$-$(CH_3)_2$N-H, 86], 75 ($CH(OMe)_2$, 60); Anal. Calcd. for $C_{10}H_{20}N_2O_3$: C, 55.56; H, 9.26; N, 12.96%. Found: 55.0; H, 9.2; N, 12.7%.

1,1-Dimethoxy-4,4-bis(piperidino)-3-buten-2-one (3j). Yellow solid, m.p.: 102-104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46-1.51 (m, 12H, $2(CH_2)_3$), 3.10 (t, *J* = 5.47 Hz, 8H, $4NCH_2$,), 3.26 (s, 6H, $2OCH_3$), 4.33 (s, 1H, C**H**$(OMe)_2$, 4.60 (s, 1H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.5 (CH_2), 25.7 (CH_2), 50.8 (NCH_2), 53.9 (OCH_3), 81.5 (=CH), 105.0 **C**$H(OMe)_2$, 168.4 (**C**=CH), 185.4 (C=O); IR (KBr, cm^{-1}) υ 2969, 2851, 1611, 1501, 1442, 1267, 1116, 752; MS (EI, 70 eV) *m/z* (%) 265 (M^+-31, 4), 221 [M^+-$CH(OMe)_2$], 88), 138 [M^+-$C(OMe)_2$-$C_5H_{10}N$, 100], 110 [M^+-$CH(OMe)_2$ -$C_5H_{10}N$-CO, 37], 84 ($C_5H_{10}N$, 99); Anal. Calcd. for $C_{16}H_{28}N_2O_3$: C, 64.86; H, 9.46; N, 9.46%. Found: C, 64.0; H, 9.3; N, 9.1%.

1,1-Dimethoxy-4,4-bis(morpholino)-3-buten-2-one (3k). Yellow solid, m.p.: 51-53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.10 (s, 8H, $4NCH_2$), 3.22 (s, 6H, $2OCH_3$), 3.58 (s, 8H, 4 OCH_2), 4.29 (s, 1H, C**H**$(OMe)_2$, 4.65 (s, 1H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.1 (4 NCH_2), 54.0 ($2OCH_3$), 66.4 (4 OCH_2), 81.7 (=CH), 104.9 $CH(OMe)_2$, 166.6 (C=CH), 186.9 (C=O); IR (KBr, cm^{-1}) υ 2926, 2851, 1608, 1501, 1444, 1050, 748; MS (EI, 70 eV) *m/z* (%) 285 (M^+-CH_3, 2), 225 [M^+-$CH(OMe)_2$], 97), 140 [M^+-$C(OMe)_2$-C_4H_8NO, 100], 86 (C_4H_8NO, 87); Anal. Calcd. for $C_{14}H_{24}N_2O_5$: C, 56.00; H, 8.00; N, 9.33%. Found: C, 55.3, H, 7.8, N, 9.2%.

RESULTS AND DISCUSSION

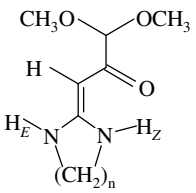
The reaction of α-oxoketene dithioacetal **1** [16] with an excess of appropriate amines proceeded easily in a reasonable volume of acetonitrile (3 mmol **1** in 10 ml acetonitrile) at room temperature. When the reaction mixture was diluted further or the amount of the added amine was less than that shown in Table 1, some of the starting material **1** remained even after prolonged stirring. Using these conditions all primary and secondary aliphatic amines (except methylamine) in the reaction with **1** yielded the corresponding α-ketene-*N,S*- or *N,N*-acetals, **2** or **3**, exclusively (Scheme 2 and Table 1).



1 **2** **3**

Scheme 2

Due to its low hindrance in the molecules of the product, aqueous methylamine reacted with **1** to give a mixture of α-oxoketene-*N,S*- and *N,N*-acetals **2a** and **3a**. The relative amounts of **2a** and **3a** depended on the amount of the added amine and did not change even after a prolonged reaction time. Aliphatic diamines, such as 1,2-diaminoethane and 1,3-diaminopropane, yielded the heterocyclic aminals **3g** and **3h**, respectively (Scheme 3).



3g; n : 2
3h; n : 3

Scheme 3

The aromatic amines were less reactive, but when the reaction mixture was refluxed, compound **1** was converted into the corresponding ketene-*N,S*-acetals **2e** and **2f** in good yields.

Secondary aliphatic amines reacted with dithioacetal **1** under the same conditions, which resulted, surprisingly, in the

Table 1. Preparation of α-Oxoketene-*N,S*- and *N,N*-Acetals **2** and **3**

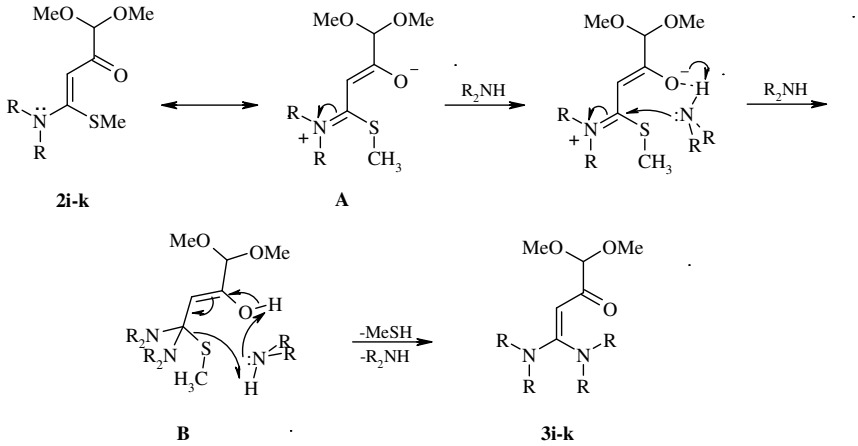
Entry	R	R´	Amine (mol equiv.)	Reaction time (h)	**2** (%)[a]	**3** (%)[a]
A	CH_3	H	10[b]	8	60	28
B	CH_3CH_2	H	10[b]	18	85	-
C	$CH_3(CH_2)_3$	H	10	24	73	-
D	$C_6H_5CH_2$	H	10	24	78	-
E	C_6H_5	H	5	6	64[c]	-
F	4-$CH_3C_6H_4$	H	5	6	72[c]	-
G	$(CH_2)_2$	H	10	14	-	87
H	$(CH_2)_3$	H	10	20	-	77
I	CH_3	CH_3	10[b]	8	-	79
J	$(CH_2)_5$		10	24	-	92
K	$CH_2CH_2OCH_2CH_2$		10	24	-	99

[a]Yields based on the isolated pure products after column chromatography (silica gel; EtOAc/petroleum ether (1:1)). [b]Aqueous solutions of methylamine (35%), dimethylamine (40%) and ethylamine (70%) were used. [c]The reaction was conducted under reflux.

Table 2. Reactions of α-Oxoketene Dithioacetal **1** with Dimethylamine[a]

Experiment No.	Dimethylamine (eq.)	Reaction time (h)	Unreacted **1** (%)[b]	**3i** (%)[b]
1	0.5	48	68	12
2	1.2	48	52	27
3	2.0	48	33	41
4	5.0	48	-	85
5	10.0	8	-	79

[a]Aqueous solution of dimethylamine (40%) was used. [b]Yields based on the isolated pure products after column chromatography (silica gel; EtOAc/ petroleum ether (1:1)).



Scheme 4

double-substitution products **3i-k** exclusively in excellent yields (Table 1). Attempts to prepare the corresponding mono-substituted products under various conditions were unsuccessful. Ila and Junjappa [11] have reported similar results using other conditions. In order to investigate this phenomenon, we carried out the reaction of dithioacetal **1** with various amounts of dimethylamine (0.5, 1.2, 2.0, 5.0, and 10.0 mol equivalents), however, in all cases, the double-substituted aminal **3i** was obtained as an exclusive product. In the reactions with lower proportions of dimethylamine (0.5, 1.2, 2.0 mol equivalents), most of the starting material **1** was recovered unchanged (see Table 2).

In order to explain these observations, it is necessary to conclude that the intermediates α-oxoketene-*N,S*-acetals **2i-k** are more reactive than the starting material **1** under the reaction conditions and react faster than **1** with another secondary amine molecule to produce the corresponding *N,N*-acetals **3i-k**. Our findings show that the presence of a secondary amine group at the α-position of the enone not only does not reduce the electrophilic character of this position but actually raises the reactivity compared to that of **1**.

Our suggested mechanism to explain this phenomenon is depicted in Scheme 4. The extensive conjugation in α-oxoketene-*N,S*-acetals **2i-k** results in a substantial negative charge on the oxygen. Because of the hydrogen bond between the negatively charged oxygen in (**A**) and the secondary amine

Table 3. ^{13}C and ^{1}H NMR Data in ($CDCl_3$) of α-Oxoketene-*N,S*- and *N,N*-Acetals **2, 3**

Entry	**C**=O δ (ppm)	C=**C**H δ (ppm)	**C**=CH δ (ppm)	C=C**H** δ (ppm)	N_E***H*** δ (ppm)	N_Z**H** δ (ppm)
2a	186.5	85.2	171.9	5.37	-	11.42
2b	186.5	85.1	170.6	5.22	-	11.33
2c	186.4	85.1	170.8	5.27	-	11.49
2d	187.0	85.9	170.8	5.39	-	11.84
2e	188.3	87.7	169.6	5.59	-	13.05
2f	187.8	87.2	169.5	5.50	-	12.91
3a	182.6	75.3	163.1	4.70	5.92	10.32
3g	185.4	74.4	165.9	5.04	6.5[a]	9.5[a]
3h	185.6	77.1	159.6	4.76[a]	8.0-9.5[a]	
3i	184.5	81.4	168.1	4.55	-	-
3j	185.4	81.5	168.4	4.60	-	-
3k	186.9	81.7	166.6	4.65	-	-

[a]Broad signal.

N-hydrogen, addition of the secondary amine takes place readily to give the intermediate (**B**). This intermediate is expected to convert to the final products **3i-k**, with the loss of methanthiol assisted by the contribution of another amine molecule. The greater reactivity of *N,S*-acetals **2i-k** over the starting material **1** can be attributed to the enhanced electrophilic character of the molecule at the β-carbon due to delocalization of the nitrogen lone pair (mesomeric form **A**) with a concomitant relative increase in the basic strength of the negatively charged oxygen, which allows it to act as an internal general base to raise the nucleophilicity of the secondary amine. The strength of this basicity is in accordance with the predominance of *O*-protonation in enaminones [17]. In the case of α-oxoketene-*S,S*-acetal **1**, delocalization of a sulfur lone pair is much less significant, since it has a relatively unfavorable overlap of sulfur 3p orbitals with carbon 2p orbitals [18].

Some ^{13}C and ^{1}H NMR data of the compounds **2a-f, 3a** and **3g-k** are given in Table 3. In the case of ketene-*N,S*-acetals **2a-f**, the strongly deshielded signal of the amine proton in the range δ 11.42-13.05 ppm, due to the intramolecular hydrogen bonding between NH and C=O, indicates that the stereochemistry of the double bond is *E* as shown in **II** in Scheme 1. For most of the α-oxoketene-*N,S*-acetals, we were not able to reveal any clear bond for new υ N-H due to the strength and symmetry of the intramolecular hydrogen bond, which results in a weak dipole [19]. As can be seen in Table 3, the chemical shifts of the carbon atoms **C**=CH (δ 159.6-171.9), C=**C**H (δ 74.4-87.7) and the corresponding proton C=C**H** (δ 4.55-5.59) are strongly dependent on the electron-donating ability of heteroatoms at the β-position.

The results show that this procedure is a facile and effective method for the selective preparation of α-oxoketene-*N,S*- and *N,N*-acetals in good to excellent yields under moderate conditions from ketene dithioacetals. On the basis of this method, moderate conditions, including an excess of added amine in a reasonable volume of acetonitrile, were used to convert selectively primary and secondary amines into the corresponding α-oxoketene-*N,S*-acetals and α-oxoketene-*N,N*-acetals, respectively. Since these compounds are used as intermediates in synthesizing various heterocyclic compounds, this convenient method is an effective means to improve total yields of the target molecules.

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