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# A highly efficient and catalytic synthetic protocol for oxathioacetalization of carbonyl compounds

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This paper is dedicated to Professor H. Ila on the occasion of her 60th birthday.

**Abstract**

A variety of aldehydes and ketones can be converted easily to the corresponding 1,3-oxathiolane derivatives, on treating with 2-mercaptoethanol using a catalytic amount of bromodimethylsulfonium bromide as pre-catalyst at room temperature under solvent-free conditions. Some of the major privileges are: mild reaction conditions, high yields, no aqueous work-up and no chromatographic separation; which is highly economic and compatible in the presence of other protecting groups. Furthermore, no brominations occur either at the double bond or α to the keto position and even in the aromatic ring.


*Keywords:* Oxathioacetalization; Carbonyl compounds; Catalytic synthetic protocol

## 1. Introduction

The conversion of aldehydes or ketones to the corresponding oxathioacetal derivatives is a useful organic transformation particularly in the protection of carbonyl functionality [1]. Among the various oxathioacetal derivatives, the chiral 1,3-oxathiane, which is actually derived from (+) pulegone in three steps, is a valuable building block for the synthesis of chiral tertiary α-hydroxy aldehydes and α-hydroxy acids in high enantiomeric purity [2]. In addition, 1,3-oxathiolane is usually preferred than the corresponding 1,3-dithioacetal because of its low cost and ease of removal at the later stage. Conventionally, oxathioacetal is prepared from the corresponding carbonyl compounds on reaction with 2-mercaptoethanol by using equimolar amount of Lewis acid such as $BF_3{\cdot}OEt_2$ [3] and $ZnCl_2$ [4]. Recently some more methods have also appeared in the literature for their preparations by employing the following catalysts, e.g. TMSOTf [5], $ZrCl_4$ [6], $LiBF_4$ [7], $HClO_4$ [8], OATB [9], NBS [10], $Sc(OTf)_3$ [11], $In(OTf)_3$ [12], and TBAB [13]. However, many of these procedures have some drawbacks which are: longer reaction times, low yields, involvement of expensive catalyst, difficult handling [5] and requirement of invariably volatile organic solvent namely dichloromethane. In an endeavor to gradually change the current working practices to greener alternatives and to meet environmental demands [14], there is a need to find out better alternatives, which might work under mild, environmentally benign and cheaper reaction conditions. In continuation of our research programme to develop better and newer synthetic methodologies [15], we realized that bromodimethylsulfonium bromide, which can generate HBr in the reaction medium on reaction with alcohol [16], might be a very useful pre-catalyst for the transformation of various carbonyl compounds as 1,3-oxathiolanes. The pre-catalyst, bromodimethylsulfonium bromide, has been utilized so far for the transformations of alcohols to the corresponding bromides [16], oxidation of thiols to the disulfides [17], deprotection of dithioacetals [18] and preparation of α-bromoenones

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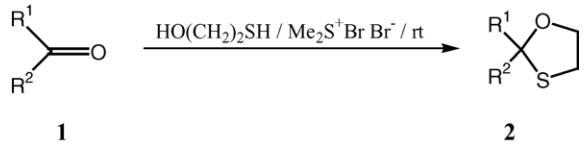



1 2

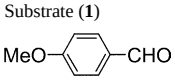
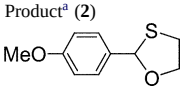
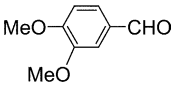
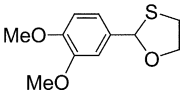
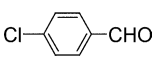
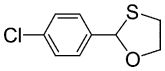
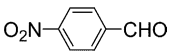
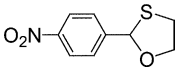
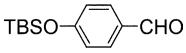
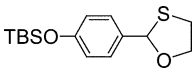
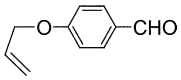
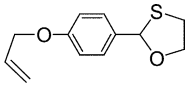
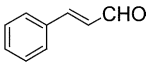
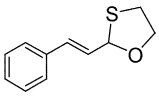
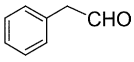
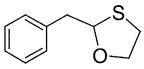
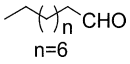
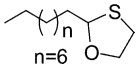
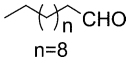
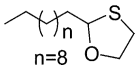
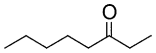
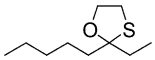
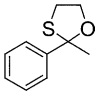
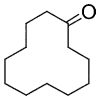
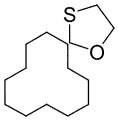
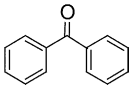
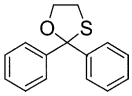
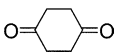
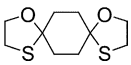
Scheme 1.

from the corresponding enones [19]. Very recently, we have demonstrated that various alcohols and phenols can be converted to the corresponding tetrahydropyranyl ethers and their deprotection to the parent hydroxyl compounds by using the same pre-catalyst [20]. These successful results prompted us to study whether the same pre-catalyst will be useful for oxathioacetalization or not. In this paper, we wish to report a very simple and practical method for the preparation of 1,3-oxathiolanes from the corresponding carbonyl compounds using a catalytic amount of bromodimethylsulfonium bromide as a new and efficient pre-catalyst under solvent-free conditions (Scheme 1).

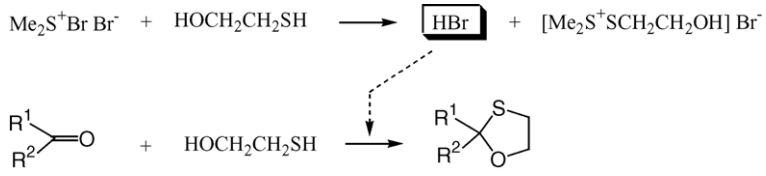
### *1.1. Result and discussion*

Firstly, bromodimethylsulfonium bromide is prepared according to the literature procedure [19]. Then we optimize the reaction conditions for the formation of oxathioacetal derivative from the corresponding carbonyl compound. It is observed that a mixture of 4-methoxybenzaldehyde (**1a**) (3 mmol) and 2-mercaptoethanol (3.1 mmol) in the presence of catalytic amount bromodimethylsulfonium bromide (0.03 mmol) provides the corresponding 2-[4′-methoxyphenyl]-1,3-oxathiolane **(2a)** within 10 min at room temperature under solvent-free conditions. The pure product **2a** is obtained by micro distillation by bulb to bulb under reduced pressure without non-aqueous work-up and chromatographic separation. The product **2a** is characterized by recording IR and $^1$H NMR spectra. The disappearance of the carbonyl frequency in the IR spectrum as well as proton signal at the aldehydic region clearly indicates the formation of the product. It is also noticed that a mixture of 4-methoxybenzaldehyde (**1a**) (30 mmol) and 2-mercaptoethanol (30 mmol) can be converted easily to the corresponding 2-[4′-methoxyphenyl]-1,3-oxathiolane **(2a)** within 10 min using 0.3 mmol of pre-catalyst under identical reaction conditions. The product **2a** is also isolated by short path distillation under reduced pressure by avoiding tedious aqueous work-up. Using above typical reaction procedures, various 1,3-oxathiolanes **2b–d** are prepared from the corresponding carbonyl compounds **1b–d** in good yields under same reaction conditions. The reactions are carried out in 30 mmol scale in most of the cases and the products are isolated by short path distillation. The oxathioacetal derivative **2d** is obtained by direct recrystallization. Likewise, 4-*tert*-butyldimethylsilyloxybenzaldehyde (**1e**) and 4-allyloxybenzaldehyde (**1f**) are converted into the corresponding 1,3-oxathiolanes derivatives **2e** and **2f** by follow-

Table 1
Preparation of various oxathioacetals **2** from the corresponding carbonyl compounds **1** using bromodimethylsulfonium bromide as pre-catalyst

| Run | Substrate (**1**) | Time min/[h] | Product[a] (**2**) | Yield[b] (%) |
|---|---|---|---|---|
| **a** |  | 10 |  | 75 |
| **b** |  | 30 |  | 70 |
| **c** |  | 10 |  | 90 |
| **d** |  | [1.5] |  | 72 |
| **e** |  | 7 |  | 78 |
| **f** |  | 7 |  | 82 |
| **g** |  | 7 |  | 74 |
| **h** |  | [1] |  | 82 |
| **I** |  | 10 |  | 73 |
| **j** |  | 15 |  | 75 |
| **k** |  | [2] |  | 86 |
| **l** |  | [12] |  | 90 |
| **m** |  | 30 |  | 97 |
| **n** |  | [1.5] |  | 90 |
| **o** |  | [2] |  | 94 |
| **p** |  | [3] |  | 92 |
| **q** |  | [12] |  | 86 |
| **r** |  | [4.5] |  | 76 |

[a] Products 2 were characterized by IR, $^1$H NMR, $^{13}$C NMR spectra and elemental analysis.
[b] Isolated yield.




Scheme 2.

ing identical conditions without affecting TBS ether and allyl groups. The reactions are carried out using 3 mmol of substrates and the products are isolated by micro distillation. Moreover, cinnamaldehyde (**1g**) and various aliphatic aldehydes **1h**–**j** are converted smoothly to the corresponding 1,3-oxathiolane derivatives **2g**–**j** in good yields, under identical reaction conditions. Furthermore, by following identical reaction procedures, an acyclic ketone **1k**, various cyclic ketones **1l**–**p** and a cyclic diketones **1q** are also transformed to the corresponding oxathioacetal derivatives **2k**–**q** in good yields. The reaction times and yields of the products are summarized in Table 1. It is worthwhile to mention that the formation of oxathioacetals from the acyclic ketones and hindered ketone such as benzophenone is a failure by $LiBF_4$ method [7]. The protected compounds are fully characterized by IR, $^1$H NMR, $^{13}$C NMR spectra and by elemental analyses. It is significant to mention that no brominations take place either at the double bond or α to the keto position and even at the aromatic ring under the experimental conditions. Notably, we have observed that the conversion of the carbonyl compounds to the respective 1,3-oxathiolane can be carried out even in a larger scale (100 mmol) without any difficulty by using 0.5 mmol of the pre-catalyst instead of 1 mmol of pre-catalyst. For example, when a mixture of 4-methoxybenzaldehyde (100 mmol) and 2-mercaptoethanol (100 mmol) was treated with 0.5 mmol of bromodimethylsulfonium bromide, it is smoothly converted to the compound **2a** in 75% yield within 10 min. From this result, it indicates that large-scale reaction might be possible even using a less amount of bromodimethylsulfonium bromide. It is worthwhile to point out that the present method is much more cleaner, does not involve any aqueous work-up, chromatographic separation and organic solvent at any stage. Moreover, turn over number (TON) is much higher in our method as compared to the earlier reported procedures [6,7,10].

The formation of the products can be explained as follows. It has been shown that bromodimethylsulfonium bromide can generate HBr in the medium on reaction with methanol [16]. We believe that HBr is generating in situ from the reaction of bromodimethylsulfonium bromide with 2-mercaptoethanol, which actually catalyzes the conversion of carbonyl compounds into the corresponding oxathioacetals (Scheme 2). It is also noted that the pH of the solution is ∼2–3 during the reaction.

The chemoselective protection of aldehyde group in the presence of a ketone can also be achieved by using 0.01 equivalent amount of the same pre-catlyst in good yield under identical conditions because of the reactivity difference between aldehyde and ketone, as depicted in Scheme 3.

## 2. Experimental

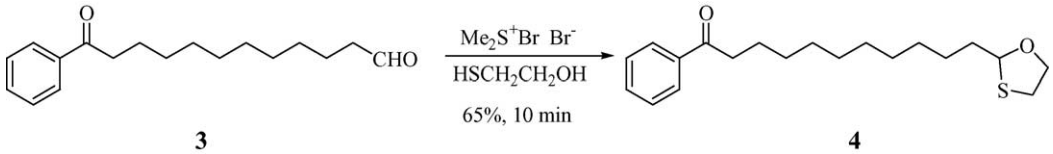
IR spectra are recorded in KBr or neat on a Nicolet Impact 410 spectrophotometer. $^1$H NMR spectra and $^{13}$C NMR spectra are recorded on a Bruker 200 or Bruker 300 or Jeol 400 MHz spectrometer in $CDCl_3$ using TMS as internal reference. Elemental analyses are carried out in a Perkin-Elmer 2400 automatic carbon, hydrogen, nitrogen and sulfur analyzer.

### 2.1. General procedure for oxathioacetalization

Into a mixture of carbonyl compound (30 mmol) and 2-mercaptoethanol (2.1 mL, 30 mmol) is added the catalyst bromodimethylsulfonium bromide (67 mg, 0.3 mmol) at room temperature and left for stirring at the same temp. After completion of the reaction as indicated by TLC, it is distilled directly to get the pure product 1,3-oxathiolane derivatives under reduced pressure.

#### 2.1.1. 2-[4′-Methoxyphenyl]-1,3-oxathiolane (2a)

Colourless liquid, 135 °C/1 mm; IR (neat) 1613, 1516, 1260, 1175, 1029, 830 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.18–3.20 (m, 1H, SC$H_a$H$_b$), 3.26–3.30 (m, 1H, SCH$_a$$H_b$), 3.80 (s, 3H, $OCH_3$), 3.87–3.94 (m, 1H, OC$H_a$H$_b$), 4.49–4.54 (m, 1H, OCH$_a$$H_b$), 5.99 (s, 1H, SCHO), 6.87 (d, 2H, $J$ = 8.6 Hz, ArH), 7.40 (d, 2H, $J$ = 8.6 Hz, ArH). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16; S, 16.34%. Found: C, 60.97; H, 6.22; S, 16.10%.




3 4

Scheme 3.

*2.1.2. 2-[3′,4′-Dimethoxyphenyl]-1,3-oxathiolane (**2b**)*

Colourless liquid, 155 °C/1 mm; IR (neat) 1599, 1511, 1463, 1383, 1264, 1229, 1140, 1048, 1021, 858 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.14–3.19 (m, 1H, $SCH_aH_b$), 3.22–3.29 (m, 1H, $SCH_aH_b$), 3.85 (s, 3H, $OCH_3$), 3.89 (s, 3H, $OCH_3$), 3.88–3.92 (m, 1H, $OCH_aH_b$), 4.48–4.52 (m, 1H, $OCH_aH_b$), 5.98 (s, 1H, SCHO), 6.80 (d, 1H, $J$ = 8.3 Hz, ArH), 6.98 (dd, 1H, $J$ = 2.0 Hz, $J$ = 8.1 Hz, ArH), 7.03 (d, 1H, $J$ = 2.0 Hz, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 33.95, 55.78, 55.86, 71.64, 87.13, 109.56, 110.58, 119.35, 131.18, 148.98, 149.30. Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.39; H, 6.24; S, 14.17%. Found: C, 58.20; H, 6.17; S, 14.01%.

*2.1.3. 2-[4′-Chlorophenyl]-1,3-oxathiolane (**2c**)*

Colourless liquid, 125 °C/5 mm; IR (neat) 1598, 1496, 1414, 1209, 1091, 1015 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.10–3.23 (m, 2H, $SCH_2$), 3.82–3.92 (m, 1H, $OCH_aH_b$), 4.41–4.54 (m, 1H, $OCH_aH_b$), 5.94 (s, 1H, SCHO), 7.30 (d, 2H, $J$ = 8.6 Hz, ArH), 7.44 (d, 2H, $J$ = 8.4 Hz, ArH). Anal. Calcd for $C_9H_9ClOS$: C, 53.86; H, 4.52; S, 15.98%. Found: C, 53.63; H, 4.59; S, 15.77%.

*2.1.4. 2-[4′-Nitrophenyl]-1,3-oxathiolane (**2d**)*

mp 78 °C; IR (KBr) 1603, 1526, 1347, 1070, 866, 717 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.21–3.30 (m, 2H, $SCH_2$), 3.99–4.06 (m, 1H, $OCH_aH_b$), 4.52–4.58 (m, 1H, $OCH_aH_b$), 6.13 (s, 1H, SCHO), 7.60 (d, 2H, $J$ = 8.7 Hz, ArH), 8.21 (d, 2H, $J$ = 8.7 Hz, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 34.08, 72.39, 85.33, 123.69 (3C), 127.12, 146.95, 147.7. Anal. Calcd for $C_9H_9NO_3S$: C, 51.17; H, 4.29; N, 6.63; S, 15.18%. Found: C, 51.29; H, 4.22; N, 6.52; S, 15.00%.

*2.1.5. 2-[4′-tert-Butyldimethylsilyloxyphenyl]-1, 3-oxathiolane (**2e**)*

Colourless liquid; IR (neat): 1608, 1511, 1265, 917, 840 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.03 (s, 6H, $Si(CH_3)_2$), 0.88 (s, 9H, $SiC(CH_3)_3$), 3.16–3.21 (m, 1H, $SCH_aH_b$), 3.22–3.29 (m, 1H, $SCH_aH_b$) 3.87–3.95 (m, 1H, $OCH_aH_b$), 4.44–4.55 (m, 1H, $OCH_aH_b$), 5.99 (s, 1H, SCHO-), 6.80 (d, 2H, $J$ = 8.5 Hz, ArH), 7.35 (d, 2H, $J$ = 8.5 Hz, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ -4.41 (2C), 18.18, 25.64 (3C), 34.03, 71.70, 87.06, 120.44 (2C), 128.18 (2C), 131.46, 156.07. Anal. Calcd for $C_{15}H_{24}O_2SSi$: C, 60.76; H, 8.16; S, 10.81%. Found: C, 60.59; H, 8.10; S, 10.63%.

*2.1.6. 2-[4′-Allyloxyphenyl]-1,3-oxathiolane (**2f**)*

Colourless liquid; IR (neat) 1649, 1613, 1511, 1419, 1301, 1239, 1173, 1024, 830 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.16–3.32 (m, 2H, $SCH_2$), 3.87–3.95 (m, 1H, $OCH_aH_b$), 4.49–4.54 (m, 3H, $OCH_aH_b$ and $CH_2OAr$), 5.28 (dd, 1H, $J$ = 1.4 Hz, $J$ = 10.5 Hz, $OCH_2HC{=}CH_aH_b$), 5.39 (dd, 1H, $J$ = 1.5 Hz, $J$ = 17.2 Hz, $OCH_2HC{=}CH_aH_b$), 5.99 (s, 1H, SCHO), 6.01–6.04 (m, 1H, $OCH_2CH{=}CH_aH_b$), 6.89 (d, 2H, $J$ = 8.7 Hz, ArH), 7.39 (d, 2H, $J$ = 8.6 Hz, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 34.01, 61.22, 71.79, 86.95, 114.61 (2C), 117.70, 118.32, 128.23 (2C), 133.05, 158.86. Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; S, 14.42%. Found: C, 64.69; H, 6.29; S, 14.21%.

*2.1.7. 2-Styryl-1,3-oxathiolane (**2g**)*

Colourless liquid, 125 °C/1 mm; IR (neat) 1496, 1445, 1268, 1200, 1059, 968, 754 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.88–2.93 (m, 1H, $SCH_aH_b$), 2.95–2.98 (m, 1H, $SCH_aH_b$), 3.89–3.92 (m, 1H, $OCH_aH_b$), 4.46–4.51 (m, 1H, $OCH_aH_b$), 5.69 (d, 1H, $J$ = 7.5 Hz, SCHO), 6.27 (dd, 1H, $J$ = 7.5 Hz, $J$ = 15.8 Hz, CH=CH-ArH), 6.60 (d, 1H, $J$ = 11.5 Hz, CH=C*H*-ArH), 7.41 (m, 5H, ArH). Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.68%. Found: C, 64.55; H, 6.35; S, 16.53%.

*2.1.8. 2-Benzyl-1,3-oxathiolane (**2h**)*

Colourless liquid, 85 °C/1 mm; IR (neat) 1603, 1495, 1454, 1265, 1084, 702 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.76 (d, 2H, $J$ = 6.4 Hz, $PhCH_2$), 2.78 (dd, 1H, $J$ = 6.4 Hz, $J$ = 9.5 Hz, $SCH_aH_b$), 2.93 (dd, 1H, $J$ = 6.6 Hz, $J$ = 13.9 Hz, $SCH_aH_b$), 3.54 (dd, 1H, $J$ = 7.3 Hz, $J$ = 14.6 Hz, $OCH_aH_b$), 4.10 (dd, 1H, $J$ = 4.6 Hz, $J$ = 9.52 Hz, $OCH_aH_b$), 5.02 (t, 1H, $J$ = 6.4 Hz, SCHO), 6.97–7.06 (m, 5H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 32.76, 42.99, 71.46, 87.41, 126.77, 128.41 (2C), 129.26 (2C), 137.51. Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; S, 17.79%. Found:C, 66.45; H, 6.75; S, 17.97%.

*2.1.9. 2-Nonyl-1,3-oxathiolane (**2i**)*

Colourless liquid; IR (neat) 1469, 1382, 1266, 1212, 1077, 1019 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 0.81 (t, 3H, $J$ = 6.6 Hz, $CH_3$), 1.11–1.19 (m, 16H, $CH_2$), 2.94–2.98 (m, 2H, $SCH_2$), 3.66–3.75 (m, 1H, $OCH_aH_b$), 4.23–4.29 (m, 1H, $OCH_aH_b$), 4.99 (t, 1H, $J$ = 6.3 Hz, SCHO). Anal. Calcd for $C_{12}H_{24}OS$: C, 66.61; H, 11.18; S, 14.82%. Found: C, 66.49; H, 11.12; S, 14.68%.

*2.1.10. 2-Undecyl-1,3-oxathiolane (**2j**)*

Colourless liquid; IR (neat) 1470, 1271, 1378, 1081 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 0.86 (t, 3H, $J$ = 6.0 Hz, $CH_3$), 1.24 (s, 20H, $CH_2$), 2.98–3.02 (m, 2H, $SCH_2$), 3.71–3.79 (m, 1H, $OCH_aH_b$), 4.28–4.34 (m, 1H, $OCH_aH_b$), 5.04 (t, 1H, $J$ = 6.4 Hz, SCHO); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 14.48, 23.05, 26.88, 29.54, 29.67, 29.74, 29.82, 29.87(2C), 32.26, 32.96, 36.84, 71.56, 87.50. Anal. Calcd for $C_{14}H_{28}OS$: C, 68.79; H, 11.55; S, 13.12%. Found: C, 68.56; H, 11.51; S, 12.96%.

*2.1.11. 2-Ethyl-2-pentyl-1,3-oxathiolane (**2k**)*

Colourless liquid, b.p. 75 °C/5 mm; IR (neat) 1465, 1378, 1265, 1065, 886 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.86 (t, 3H, $J$ = 6.9 Hz, $CH_3$), 0.96 (t, 3H, $J$ = 6.9 Hz, $CH_3$), 1.32–1.37 (m, 6H, $CH_2$), 1.73–1.87 (m, 4H, $CH_2$), 2.96 (t, 2H, $J$ = 5.9 Hz, $SCH_2$), 4.12 (t, 2H, $J$ = 5.8 Hz, $OCH_2$). Anal.

Calcd for $C_{10}H_{20}OS$: C, 63.78; H, 10.70; S, 17.03%. Found: C, 63.51; H, 10.61; S, 16.93%.

*2.1.12. [2-Methyl-2-phenyl]-1,3-oxathiolane (**2l**)*

Colourless liquid, b.p. 110 °C/5 mm [lit. b.p. 85 °C/1.2 mm[5b]]; IR (neat) 1496, 1383, 1219, 1142, 1066, 769 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.9 (s, 3H, $CH_3$), 3.05–3.10 (m, 1H, $SCH_aH_b$), 3.20–3.26 (m, 1H, $SCH_aH_b$), 4.00–4.06 (m, 1H, $OCH_aH_b$), 4.33–4.38 (m, 1H, $OCH_aH_b$), 7.30–7.47 (m, 3H, ArH), 7.48–7.50 (m, 2H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 32.36, 34.46, 70.66, 95.59, 124.84 (2C), 127.19, 128.14 (2C), 146.73. Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; S, 17.79%. Found: C, 66.46; H, 6.62; S, 17.58%.

*2.1.13. 1-Oxa-4-thiaspiro[4.4]nonane (**2m**)*

Colourless liquid, b.p. 70 °C/5 mm [lit. b.p. 35 °C/0.6 mm[5b]]; IR (neat) 1439, 1323, 1264, 1159, 1070 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.55–1.74 (m, 4H, $CH_2$), 1.91–2.05 (m, 4H, $CH_2$), 3.06 (t, 2H, $J$ = 5.8 Hz, $SCH_2$), 4.05 (t, 2H, $J$ = 5.9 Hz, $OCH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$,) $\delta$ 23.90 (2C), 33.66, 40.92 (2C), 69.74, 100.43. Anal. Calcd for $C_7H_{12}OS$: C, 58.29; H, 8.39; S, 22.23%. Found: C, 58.08; H, 8.33; S, 22.15%.

*2.1.14. 1-Oxa-4-thiaspiro[4.5]decane (**2n**)*

Colourless liquid, b.p. 85 °C/5 mm [lit. b.p. 45 °C/0.2 mm[5b]]; IR (neat) 1449, 1270, 1239, 1145, 1075, 686 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.32–1.52 (m, 4H, $CH_2$), 1.74–1.89 (m, 6H, $CH_2$), 3.00 (t, 2H, $J$ = 5.8 Hz, $SCH_2$), 4.14 (t, 2H, $J$ = 5.9 Hz, $OCH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 24.83 (2C), 25.02, 32.86, 39.94 (2C), 69.46, 96.49. Anal. Calcd for $C_8H_{14}OS$: C, 60.72; H, 8.92; S, 20.26%. Found: C, 60.53; H, 8.98; S, 20.08%.

*2.1.15. 1-Oxa-4-thiaspiro[4.6]undecane (**2o**)*

Colourless liquid, b.p. 90 °C/5 mm [lit. b.p. 77–78 °C/1.2 mm[5b]]; IR (neat) 1460, 1070 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.55–1.66 (m, 8H, $CH_2$), 1.97–2.09 (m, 4H, $CH_2$), 3.00 (t, 2H, $J$ = 5.8 Hz, $SCH_2$), 4.09 (t, 2H, $J$ = 5.9 Hz, $OCH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$,) $\delta$ 23.38 (2C), 28.48 (2C), 33.09, 43.07 (2C), 69.74, 99.71. Anal. Calcd for $C_9H_{16}OS$: C, 62.74; H, 9.36; S, 18.61%. Found: C, 62.53; H, 9.28; S, 18.42%.

*2.1.16. 1-Oxa-4-thiaspiro[4.11]hexadecane (**2p**)*

Colourless liquid, b.p. 130 °C/1 mm; IR (neat) 1465, 1440, 1065 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.35 (s, 18H, $CH_2$), 1.73–1.83 (m, 2H, $CH_2$), 1.97–2.05 (m, 2H, $CH_2$), 3.04 (t, 2H, $J$ = 6.0 Hz, $SCH_2$), 4.11 (t, 2H, $J$ = 6.1 Hz, $OCH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 20.91 (2C), 22.19 (2C), 22.42 (2C), 25.86, 26.19 (2C), 32.97, 36.09 (2C), 69.65, 99.01. Anal. Calcd for $C_{14}H_{26}OS$: C, 69.36; H, 10.81; S, 13.23%. Found: C, 69.13; H, 10.72; S, 13.11%.

*2.1.17. 2,2-[Diphenyl]-1,3-oxathiolane (**2q**)*

Colourless liquid, b.p. 120 °C/5 mm [lit. b.p. 87 °C/0.6 mm[5b]]; IR (neat) 1490, 1449, 1280, 1060 $cm^{-1}$;$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.20–3.25 (m, 2H, $SCH_2$), 4.17–4.23 (m, 2H, $OCH_2$), 7.20–7.29 (m, 5H, ArH), 7.49–7.52 (m, 5H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 34.71 (2C), 70.23 (2C), 126.69 (4C), 127.57 (2C), 128.01 (4C), 144.37. Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82; S, 13.23%. Found: C, 74.10; H, 5.72; S 13.14%.

*2.1.18. 1,9-Dioxa-4,12-dithiadispiro[4.2.4.2] tetradecane (**2r**)*

mp 73–74 °C; IR (KBr) 1439, 1357, 1280, 1234, 1168, 10.70, 891 $cm^{-1}$;$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.60–1.97 (m, 4H, $CH_2$), 2.01–2.17 (m, 4H, $CH_2$), 3.04 (t, 4H, $J$ = 5.9 Hz, $SCH_2$), 4.12 (t, 4H, $J$ = 5.8 Hz, $OCH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 33.01 (2C), 37.61 (2C), 37.71 (2C), 69.79, 69.87, 94.29 (2C). Anal. Calcd for $C_{10}H_{16}O_2S_2$: C, 51.69; H, 6.94; S, 27.60%. Found: C, 51.44; H, 6.85; S, 27.39%.

*2.1.19. Compound **4***

Liquid, IR (Neat) 2928, 2865, 1688, 1590, 1464, 1368, 1116, 780 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.30 (m, 14H, $–CH_2$), 1.74 (m, 2H, $–CH_2$), 1.78–1.85 (m, 2H, $–CH_2$), 2.92 (t, 2H, $J$ = 7.6 Hz, $COCH_2$), 3.03 (m, 2H, $SCH_2$), 3.70 (m, 1H, -$OCH_2$), 4.31 (m, 1H, $OCH_2$), 5.06 (t, 1H, $J$ = 7.2 Hz, OCHS), 7.45 (m, 2H, ArH), 7.53 (m, 1H, ArH), 7.95 (m, 2H, ArH); Anal. Calcd for $C_{20}H_{30}O_2S$ (334.52); C, 71.81; H, 9.04; S, 9.59. Found: C, 71.60; H, 9.10; S, 9.46.

## 3. Conclusion

We have devised a simple and catalytic method for the preparation of oxathioacetals from the corresponding carbonyl compounds by employing bromodimethylsulfonium bromide as the pre-catalyst without involvement of solvent at any stage. It is important to mention that neither the olefinic double bonds nor aromatic rings are brominated during the reaction conditions. In addition, aldehyde group can be protected chemoselectively in the presence of a keto group. Due to its operational simplicity, generality, efficacy and cost effectiveness, this method is expected to have wider applicability for conversion of various carbonyl compounds as oxathioacetals.

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