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Efficient Method for Thioacetalization of Carbonyl Compounds in the Presence of a Catalytic Amount of Benzyltriphenylphosphonium Tribromide (BTPTB) under Solvent-Free Conditions

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Efficient Method for Thioacetalization of Carbonyl Compounds in the Presence of a Catalytic Amount of Benzyltriphenylphosphonium Tribromide (BTPTB) under Solvent-Free Conditions

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Abstract: A variety of carbonyl compounds have been successfully converted to the corresponding thioacetal derivatives in good to excellent yields on reaction of carbonyl compounds with 1,2-ethanedithiole, 1,3-propanedithiol, and ethylthiol in the presence of a catalytic amount of benzyltriphenylphosphonium tribromide (BTPTB) under solvent-free conditions. Some of the major advantages of this method are mild reaction conditions, high efficiency, and the compatibility with other reported methods. In addition, no bromination occurs at the double bond or α to the keto position or even in the aromatic ring under these experimental conditions.

Keywords: Carbonyl compounds, solvent-free, thioacetalization

INTRODUCTION

One of the major challenging problems during multistep syntheses is protection of carbonyl functional groups from nucleophilic attack until their electrophilic nature is exploited. For this reason, the protection of carbonyl groups is essential for organic chemists. Among carbonyl

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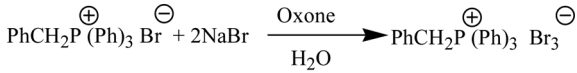
protecting groups, dithioacetals constitute an important class of compounds as acyl anion equivalents[1] or masked methylene functions in carbon–carbon bond-forming reactions. On the other hand, these substrates are versatile[2] as a result of their straightforward preparation and also their stability under basic or mildly acidic conditions. Different methods have been reported for protection of carbonyl compounds,[3–17] but many of these procedures are associated with certain limitations such as low yields, harsh reaction conditions, longer reaction times, and expensive reagents. Therefore milder, simpler, and more efficient alternatives are still desirable for protection of carbonyl compounds.

Organic ammonium tribromide (OATB)[18] is an extremely useful reagent in organic synthesis particularly for deprotection of dithioacetals,[19] natural product synthesis,[20] deprotection of tert-butyldimethylsilyl (TBDMS) ethers,[21] and protection/deprotection of tetrahydropyranyl (THP) ethers.[22] Several tribromides have been reported;[23] however, their preparation mostly involves using bromine, which in most cases causes an environmental problem.

RESULTS AND DISCUSSION

In continuation of our studies on reactions under solvent-free conditions and developing new methods for transformation of organic functional groups,[24–26] here we introduce a new and environmentally benign method for the synthesis of benzyltriphenylphosphonium tribromide (BTPTB) **1** and application of this reagent as a mild and efficient catalyst for protection of the carbonyl functional group.

Reagent **1** has been synthesized by dropwise addition of a solution of inexpensive and commercially available Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) to a solution of benzyltriphenylphosphonium bromide and NaBr in water at room temperature to afford a yellow precipitate in quantitative yields that showed an intense electronic absorbtion at 279 nm typical of tribromide (Scheme 1).[18] Reagent **1** is a very stable compound and can be stored for months without losing its activity. This reagent also is a highly chemoselective catalyst for the conversion of aldehydes in the presence of ketones to the corresponding dithioacetals under solvent-free conditions.



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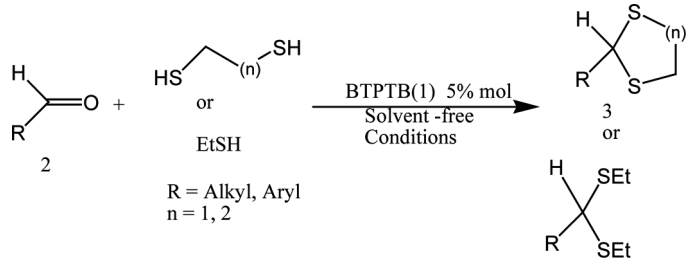
Scheme 1.



Scheme 2.

Initially we tried the protection of aldehydes **2** to the corresponding dithioacetals **3** by 1,2-ethanedithiole, 1,3-propanedithiol, and ethylthiol l in a mortar in the presence of 5 mol% of BTPTB at room temperature under solvent-free conditions. This reaction gave dithioacetal derivatives in 90–98% yield after 3–7 min. The reaction was tried using wide variety of aldehydes containing electron-withdrawing and electron-donating substituents. The protection of heteroaromatic and α,ß-unsaturated aldehydes also was carried out under similar reaction conditions (Scheme 2, Table 1). The reaction proceeds efficiently for aldehydes at ambient temperature in essentially mild and almost neutral conditions. The reaction in the absence of BTPTB did not occurred at all even under heating conditions at 60 °C for 10 h. The reaction also has been employed for protection of aldehydes with acid-sensitive substrate such as furfural as its dithioacetals derive in almost quantitative yield without the formation of any side products. In addition, no bromination occurs at the double bond or α to the keto position or even in the aromatic ring under these experimental conditions.

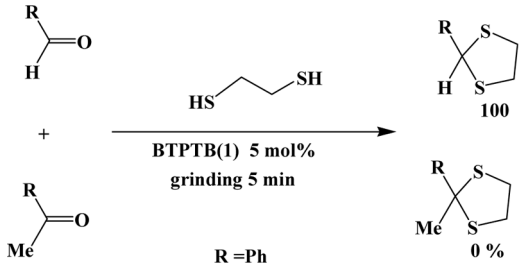
The thoacetalization of ketone **4** with 1,2-ethanedithiol under solvent-free conditions was carried out in the presence of 5 mol% of BTPTB to afford product **5**. As shown in Table 2, in comparison to aldehydes, the reaction times for protection of ketones are longer (1–2 h) (Table 2, Scheme 3).

Moreover, this procedure is highly chemoselective, providing selective protection of an aldehyde in the presence of a ketone. Treatment of an equimolar mixture of benzaldehyde and acetophenone in the presence of 1,3-ethanedithiol and a catalytic amount of reagent **1** (5 mol%) under solvent-free conditions produced only 1,3-dithiolane derivative of benzaldehyde with complete recovery of the acetophenone, thus illustrating the chemoselectivity of the present method [Eq. (1), Scheme 4]. The other competition reactions are shown in Eqs. (1–3).

Table 1. Thioacetalization of aldehyde **2** with reagent **1** under solvent-free conditions[a,b]

Entry	Substrate	Protecting group	Time (sec)	Yield (%)[b]
2a	Ph	$HS(CH_2)_3SH$	50	97
2b	Ph	$HS(CH_2)_2SH$	70	95
2c	4-$(NO_2)C_6H_4$	SEt	70	95
2d	4-(Cl)C_6H_4	$HS(CH_2)_2SH$	50	90
2e	4-(MeO)C_6H_4	SEt	50	90
2f	4 $(Me_2N)C_6H_4$	SEt	40	90
2g	2-(MeO)C_6H_4	$HS(CH_2)_2SH$	70	98
2h	3-(MeO)C_6H_4	$HS(CH_2)_2SH$	40	98
2i	4-(TBSO)C_6H_4	$HS(CH_2)_3SH$	60	98
2j	4-(AllylO)C_6H_4	$HS(CH_2)_3SH$	50	97
2k	4-(Cyclohexyl)C_6H_4	$HS(CH_2)_3SH$	45	98
2l	4(BzO)C_6H_3	$HS(CH_2)_3SH$	40	98
2m	$PhCH_2$	$HS(CH_2)_3SH$	50	95
2n	4-(OH)C_6H_4	$HS(CH_2)_3SH$	50	93
2o	2-Furyl	$HS(CH_2)_3SH$	40	98
2p	4-$(O_2N)C_6H_4$	$HS(CH_2)_2SH$	45	90
2q	PhCH=CH	$HS(CH_2)_3SH$	60	90
2r	n-C_6H_{13}	$HS(CH_2)_2SH$	50	90
2s	TBDPSO-n-C4H8	$HS(CH_2)_3SH$	50	94
2t	4-(MeO)C_6H_4	$HS(CH_2)_2SH$	60	98
2u	4-(Me)C_6H_4	$HS(CH_2)_2SH$	45	97
2v	4-(OH)C_6H_4	$HS(CH_2)_2SH$	60	98
2w	4-(OH)-2-(MeO)C_6H_4	$HS(CH_2)_2SH$	50	94
2x	4 $(Me_2N)C_6H_4$	$HS(CH_2)_2SH$	80	91
2y	3-Formyl-hexane	$HS(CH_2)_2SH$	50	94
2z	2,5-$(MeO)_2C_6H_3$	$HS(CH_2)_3SH$	45	92

[a]Confirmed by comparison with authentic samples (TLC, GC, IR, and ^{1}H NMR).
[b]Yield of isolated pure product after purification.

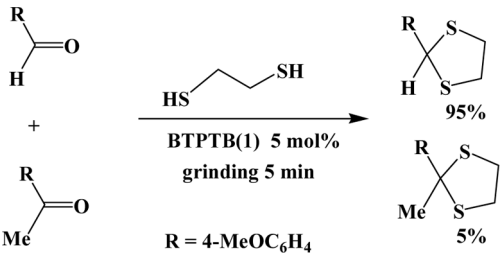


(1)

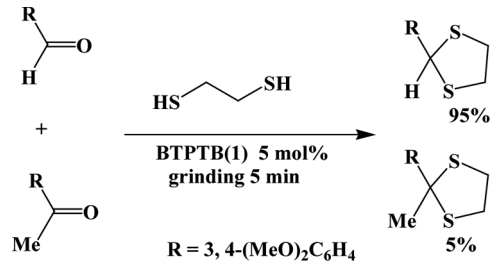
Table 2. Thioacetalization of ketones **4** with reagent **1** under solvent-free conditions at room temperature[a,b]

Subtrate	R^1		R^2	Time (h)	Yield (%)[c]
4a	Ph		Me	1.5	98
4b	4-(Me)C_6H_4		Me	1.7	93
4c	4-(Me)C_6H_4		Ph	1.3	93
4d	4-(OH)C_6H_4		Me	1.5	98
4e	4-(Cl)C_6H_4		Me	1.5	95
4f	$C_6H_4CH_2$		Me	1.5	97
4g	Ph		Ph	1.5	91
4h	4-(Br)C_6H_4		Me	2.0	94
4i		$-(CH_2)_4-$		2.0	91
4j	n-Pen		Et	2.0	94
4k		$-(CH_2)_6-$		1.5	96
4l		$-(CH_2)_5-$		2.0	93
4m	$CH_3(CH_2)_4$		Me	1.5	96
4n	$CH_3(CH_2)_2$		$CH_3(CH_2)_2$	1.5	97

[a]Confirmed by comparison with authentic samples (TLC, GC, IR, and NMR).
[b]Molar ratio of **1:4** (1:1).
[c]Yield of isolated pure product after purification.



(2)



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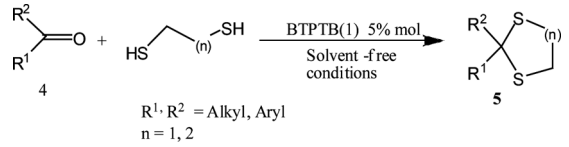


Scheme 3.

The possible mechanism is shown in Scheme 4. Initially the reagent **1** reacts with the 1,2-ethandithiol to generate HBr as catalyst, and the producing HBr activates the carbonyl group for further reaction with dithiol to form a hemithioacetal-type intermediate, which by losing the HOBr molecule affords the corresponding carbonyl derivatives (Scheme 4), and HBr activates the carbonyl compounds again for further reaction.

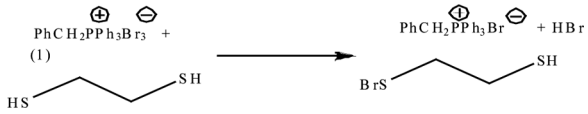
Another noteworthy aspect of this reagent is that this reagent is reproducible. To recover the reagent, after finishing the reaction and isolating the product by ether, the residue was dissolved in water and treated with new bath of Oxone® and NaBr to produce the reagent again. Therefore this method is also important from the point of view of green chemistry.

In summary, we report here an efficient method for protection of aldehydes and ketones with 1,4-ethanedithol to the corresponding 1,3-dithiolane under solvent-free conditions. This procedure is an efficient method for protection of aliphatic and aromatic ketone; the yields of products are high, and the reaction time is low. The reagent is stable and may be kept for months without losing its activity. This reagent is reproducible and also handles easily.

EXPERIMENTAL

General

All yields refer to isolated products after purification. All of the products were characterized by comparison of their spectral (IR, ^{1}H NMR, TLC, and GC) and physical data (melting and boiling points) with those of



Scheme 4.

authentic samples. All ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ relative to TMS as an internal standard. All ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ relative to TMS as an internal standard. All of the reactions were carried out in a mortar in a hood with strong ventilation.

Procedure for the Preparation of Benzyltriphenylphosphonium Tribromide

To a solution of benzyltriphenylphosphonium bromide (0.01 mol, 3.88 g) and sodium bromide (0.043 mol, 4.37 g) in water (100 ml), a solution of Oxone® ($4KHSO_5 \cdot KHSO_4 \cdot K_4SO_4$) (0.044 mol, 13.65 g) in water (40 ml) was added dropwise under stirring at room temperature until a yellow precipitate was formed. After stirring for 30 min, the mixture was filtered and washed with water (3×30 ml). The filter cake was dried and recrystallized from $CHCl_3$ to afford BTPTB as yellow crystals (4.15 g, 70% yield), mp: 136–137 °C. IR (KBr) υ: 3050 (m), 4950 (s), 1580 (s), 1115 (s), 900 (m) cm^{-1}. ^{1}H NMR: δ 7.44–7.98 (m, 40H) 4.90 (d, $J = 18$ Hz, 4H), UV (CH2C2) λ_{max}: 479 nm. Anal. calcd. for $C_{45}H_{44}Br_3P$: C, 50.84%; H, 3.74%. Found: C, 50.74%; H, 3.60%.

Thioacetalization under Solvent-Free Conditions

In a mortar, aldehyde or ketone (10 mmol) was added to a mixture of 1,2-ethandithiol, 1,3-propandithiol, or ethylthiol (14 mmol) and BTPTB (0.5 mmol 0.3 g). The reaction mixture was ground by pestle at room temperature under solvent-free conditions. After disappearance of starting material (monitored by thin-layer chromatography, TLC), the mixture was washed with diethyl ether and filtered. The filtrate was evaporated under reduced pressure, and the resulting crude material was purified by column chroatography (EtoAc–n-hexane) to afford pure dithioactas (Tables 1 and 2).

Data

2-Phenyl-1,3-dithiane (3a)[27]

White solid; mp 74 °C; IR (KBr): 3037, 2940, 2894, 2827, 1593, 1491, 1429, 1281, 1183, 1066, 912, 728, 697 cm^{-1}. ^{1}H NMR: $\delta = 1.85$–1.96 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.09–2.16 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.85–2.90 (m, 2 H, SCH_2), 2.99–3.07 (m, 2 H, SCH_2), 5.16 (S, 1 H, ArCH), 7.24–7.35 (m, 3 H, ArH), 7.45–7.47 (m, 2 H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 24.96$, 31.95 (2 C), 51.34, 127.61

(2 C), 128.29, 128.59 (2 C), 138.99 ppm. Anal calcd. for $C_{10}H_{12}S_2$ (196.34): C, 61.17; H, 6.16; S, 32.66%. Found: C, 61.95; H, 6.14; S, 32.49%.

2-Phenyl-1,3-dithiolane (3b)[17]

IR (neat): 3429, 3060, 3026, 2922, 1690, 1661, 1600, 1494, 1451, 1422, 1276 cm^{-1}. ^1H NMR: $\delta = 3.23$–3.46 (m, 4 H), 5.61 (s, 1 H), 7.19–7.30 (m, 3 H), 7.49 (d, $J = 7.10$ Hz, 2 H). ^{13}C NMR: $\delta = 40.81$ (2 CH_2), 56.82, 128.52, 128.56, 129.02, 140.94.

3-Nitrobenzaldehyde Dethylthioacetal (3c)[17]

Light yellow oil. ^1H NMR : $\delta = 8.28$ (br d, $J = 1.5$ Hz, 1 H), 8.12 (br dd, $J = 8.0$, 1.5 Hz, 1 H), 7.80 (br dd, $J = 8.0$, 1.5 Hz, 1 H), 7.52 (t, $J = 8.0$ Hz, 1 H), 4.92 (s, 1 H), 2.58–2.46 (m, 4 H), 1.22 (t, $J = 7.0$ Hz, 6 H).EIMS: $m/z = 257$ (M^+), 196, 168, 121. Anal. calcd. for $C_{11}H_{15}NO_2S_2$: C, 51.36; H, 7.55; N, 5.45. Found: C, 51.55; H, 7.72; N, 5.38.

2-(4-Chlorophenyl-1,3-dithiolane (3d)[28]

IR (neat): 3006, 2903, 1486, 1404, 1085, 1012, 754 cm^{-1}. ^1H NMR: $\delta = 3.20$–3.70 (m, 4 H), 5.58 (s, 1 H), 7.31 (d, $J = 8.4$ Hz, 2 H), 7.41 (d, $J = 8.4$ Hz, 2 H). ^{13}C NMR: $\delta = 40.27$ (2 CH_2), 55.44, 128.57, 129.30, 133.61, 139.02.

4′-Methoxyphenyl Diethyl Dithioacetal (3e)[28]

White solid; mp 43 °C; IR (KBr): 2965, 2928, 1609, 1510, 1447, 1301, 1261, 1174, 1106, 1025 cm^{-1}. ^1H NMR: $\delta = 1.22$ (t, $J = 7.3$ Hz, 6 H, $2 \times SCH_2CH_3$), 2.46–2.63 (m, 4 H, $2 \times SCH_2CH_3$), 3.80 (s, 3 H, OCH_3), 4.91 (s, 1 H, ArCH), 6.85 (d, $J = 8.6$ Hz, 2 H, ArH), 7.37 (d, $J = 8.5$ Hz, 2 H, ArH) ppm. ^{13}C NMR: $\delta = 14.24$ (2 C), 26.15 (2 C), 51.69, 55.22, 113.75 (2 C), 128.77 (2 C), 132.37, 159.00 ppm. Anal. calcd. for $C_{12}H_{18}OS_2$ (242.41): C, 59.46; H, 7.48; S, 26.46%. Found: C, 59.60; H, 7.50; S, 26.20%.

4-*N,N*-Dimethylbenzaldehyde Diethylthioacetal (3f)

Light yellow oil. ^1H NMR: $\delta = 7.30$ (d, $J = 8.0$ Hz, 2 H), 6.68 (d, $J = 8.0$ Hz, 2 H), 4.86 (s, 1 H), 2.98 (s, 6 H), 2.62–2.43 (m, 4 H),

1.16 (t, $J = 7.0$ Hz, 6 H). EIMS: $m/z = 255$ (M^+), 240, 194, 179, 120. Anal. calcd. for $C_{13}H_{21}NS_2$: C, 61.18; H, 8.24; N, 5.49. Found: C, 61.32; H, 8.17; N, 5.33.

2-(2-Methoxypheny-1,3-dithiolane (3g)[17]

IR (neat): 3038, 2999, 2923, 2833, 1597, 1488, 1464, 1434, 1316, 1263, 1149, 1047, 862, 779, 749, 693 cm^{-1}. ^1H NMR: $\delta = 3.10$–3.45 (m, 4 H), 3.73 (s, 3 H), 5.58 (s, 1 H), 6.76 (d, $J = 7.32$ Hz, 1 H), 7.05–7.21 (m, 3 H). ^{13}C NMR: $\delta = 40.04$ (2 CH_2), 55.08, 56.04, 113.34 (2 C), 120.14, 129.32, 141.91, 159.45.

2-(2-Methoxypheny 1,3-Dithiolane (3h)[17]

IR (neat): 3068, 2921, 2777, 1609, 1500, 1487, 1443, 1370, 1249, 1183, 1096, 1038, 927, 866, 750 cm^{-1}. ^1H NMR: $\delta = 3.25$–3.53 (m, 4 H), 5.60 (s, 1 H), 5.94 (s, 2 H), 6.69 (d, $J = 8$ Hz, 1 H), 6.91–6.95 (dd, $J = 8$, 1.7 Hz, 1 H), 7.10 (d, $J = 1.7$ Hz, 1 H). ^{13}C NMR: $\delta = 40.24$ (2 CH_2), 56.35, 101.20, 107.73, 108.32, 121.35, 133.88, 147.46, 147.85.

2-(4-*tert*-Butyldimethylsilyloxyphenyl)-1,3-dithiane (3i)[17]

^1H NMR: $\delta = 0.19$ (s, 6 H), 0.97 (s, 9 H), 3.26–3.35 (m, 2 H), 3.40–3.66 (m, 2 H), 6.76 (d, $J = 8.5$ Hz, 2 H), 7.38 (d, $J = 8.5$ Hz, 2 H). ^{13}C: $\delta = -4.2$, 19.5, 27.6, 40.5, 57.3, 120.8, 131.7, 134.5, 156.3. MS: m/z = 313 ($M + H^+$). Anal. calcd. for $C_{15}H_{24}OS_2Si$: C, 57.64; H, 7.74%. Found: C, 57.60; H, 7.70%.

2-(4′-Allyloxyphenyl)-1,3-dithiane (3j)[17]

White solid; mp 81 °C; IR (KBr): 2914, 1603, 1506, 1429, 1245, 1183, 1015, 779 cm^{-1}. ^1H NMR: $\delta = 1.84$–1.97 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.11–2.17 (m, 1 H, $SCH_2CH_aH_b$ CH_2S), 2.86–2.91 (m, 2 H, SCH_2), 3.00–3.14 (m, 2 H, SCH_2), 4.50–4.52 (m, 2 H, $OCH_2CH{=}CH_2$), 5.13 (s, 1 H, ArCH), 5.27 (dd, $J = 3.0$, $J = 10.6$ Hz, 1 H, $OCH_2CH{=}CH_aH_b$), 5.39 (dd, $J = 3.2$, $J = 17.1$ Hz, 1 H, $OCH_2CH{=}CH_aH_b$), 5.98–6.08 (m, 1 H, $OCH_2CH{=}CH_aH_b$), 6.87 (d, $J = 8.8$ Hz, 2 H, ArH), 7.38 (d, $J = 8.8$ Hz, 2 H, ArH) ppm. ^{13}C NMR: $\delta = 24.97$, 32.10 (2 C), 50.66, 68.81, 114.86 (2 C), 118.26, 128.86 (2 C), 131.34, 133.03, 158.49 ppm. Anal. calcd. for $C_{13}H_{16}OS_2$ (252.40): C, 61.86; H, 6.39; S, 25.41%. Found: C, 61.60; H, 6.30; S, 25.20%.

2-(4′-(Cyclohexenyloxy)phenyl)-1,3-dithiane (3k)[17]

White solid; mp 103–104 °C; IR (KBr): 2933, 1605, 1509, 1242, 1168 cm^{-1}. ^1H NMR: $\delta = 1.57$–1.65 (m, 2 H, CH_2), 1.76–1.89 (m, 2 H, CH_2), 1.91–2.03 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.05–2.18 (m, 3 H, $SCH_2CH_aH_b$ CH_2S and CH_2), 2.84–2.92 (m, 2 H, SCH_2), 3.01–3.15 (m, 2 H, SCH_2), 3.54–3.55(m, 1 H, CH=CHCHO), 5.10 (s, 1 H, ArCH), 5.81 (dd, $J = 2.0$, $J = 10.0$ Hz, 1 H, CH=CHCHO), 6.03–6.08 (m, 1 H, CH_2CH=CHCHO), 6.87 (d, $J = 8.8$ Hz, 2 H, ArH), 7.37 (d, $J = 8.8$ Hz, Hz, 2 H, ArH) ppm. ^{13}C NMR: $\delta = 21.37$, 24.93, 25.04, 29.80, 32.24 (2 C), 38.08, 50.94, 116.38, 126.87, 128.95, 129.36, 131.00, 131.18 (2 C), 154.14 ppm. Anal. calcd. For $C_{16}H_{20}OS_2$ (292.47): C, 65.71; H, 6.89; S, 21.93. Found: C, 65.52; H, 6.81; S, 21.79.

2-(4′-(Benzoyloxy)phenyl)-1,3-dithiane (3l)[17]

Mp 163–164 °C; IR (KBr): 3068, 2955, 2894, 1731, 1593, 1506, 1424, 1265, 1204, 1168, 1071, 1020, 886, 769, 707 cm^{-1}. ^1H NMR: $\delta = 1.88$–1.98 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.15–2.18 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.89–2.93 (m, 2 H, SCH_2), 3.03–3.09 (m, 2 H, SCH_2), 5.20 (S, 1 H, ArCH), 7.20 (d, $J = 8.8$ Hz, 2 H, ArH), 7.51 (m, 2 H, ArH), 7.53 (d, $J = 8.5$ Hz, 2 H, ArH), 7.63 (m, 1 H, ArH), 8.18 (m, 2 H, ArH) ppm. ^{13}C NMR: $\delta = 25.04$, 32.03 (2 C), 50.72, 121.95 (2 C), 128.57 (2 C), 129.03 (2 C), 129.43, 130.17 (2 C), 133.64, 136.74, 150.80, 164.95 ppm. Anal. calcd. for $C_{17}H_{16}O_2S_2$ (316.44): C, 64.53; H, 5.10; S, 20.27%. Found: C, 64.40; H, 5.00; S, 20.00%.

2-Benzyl-1,3-dithiolane (3m)

Colorless liquid; IR (neat): 3037, 2925, 2843, 1598, 1501, 1424, 1286, 1132, 1030, 846, 738 cm^{-1}. ^1H NMR: $\delta = 3.04$ (d, $J = 7.1$ Hz, 2 H, $PhCH_2$), 3.08–3.21 (m, 4 H, $2 \times SCH_2$), 4.66 (t, $J = 7.1$ Hz, 1 H, $PhCH_2CH$), 7.16–7.26 (m, 5 H, ArH) ppm. Anal. calcd. for $C_{10}H_{12}S_2$ (196.34): C, 61.17; H, 6.16; S, 32.66%. Found: C, 61.30; H, 6.10; S, 32.40%.

2-(4′-Hydroxyphenyl)-1,3-dithiane (3n)[14]

Mp 158 °C; IR (KBr): 3370, 2940, 2894, 2807, 1609, 1516, 1450, 1363, 1250, 1173, 1112, 851, 774 cm^{-1}. ^1H NMR: $\delta = 1.85$–1.96 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.12–2.19 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.86–2.92 (m, 2 H, SCH_2), 3.01–3.08 (m, 2 H, SCH_2), 5.12 (S, 1 H, ArCH), 6.77

(d, $J = 8.2$ Hz, 2 H, ArH), 7.31 (d, $J = 8.3$ Hz, 2 H, ArH) ppm. ^{13}C NMR: $\delta = 25.06$, 32.18 (2 C), 50.74, 115.58 (2 C), 129.18 (2 C), 131.45, 155.61 ppm. Anal. calcd. for $C_{10}H_{12}OS_2$ (212.34): C, 56.56; H, 5.70; S, 32.20%. Found: C, 56.30; H, 5.60; S, 32.00%.

2-Furfuryl-1,3-dithiane (3o)[29]

Pale yellow liquid; IR (neat): 2899, 1495, 1424, 1275, 1163, 1014, 748 cm^{-1}. ^{1}H NMR: $\delta = 1.92$–2.01 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.08–2.16 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.88–2.93 (m, 4 H, $2 \times SCH_2$), 5.20 (s, 1 H, SCHS), 6.32 (dd, $J = 2.0$, $J = 3.2$ Hz, 1 H, H-4), 6.37 (d, $J = 3.1$ Hz, 1 H, H-3), 7.34 (d, $J = 1.9$ Hz, 1 H, H-5) ppm. ^{13}C NMR: $\delta = 25.22$, 30.24 (2 C), 41.99, 107.83, 110.56, 142.27, 151.66 ppm. Anal. calcd. for $C_8H_{10}OS_2$ (186.30): C, 51.58; H, 5.41; S, 34.42%. Found: C, 51.40; H, 5.30; S, 34.20%.

2-(4′-Nitrophenyl)-1,3-dithiolane (3p)

Yellow low-melting solid; IR (neat): 2930, 2853, 1603, 1521, 1424, 1352, 1317, 1291, 1245, 1112, 1015, 984, 876, 830, 784 cm^{-1}. ^{1}H NMR: $\delta = 3.37$–3.43 (m, 2 H, SCH_2), 3.45–3.55 (m, 2 H, SCH_2), 5.65 (s, 1 H, ArCH), 7.66 (d, $J = 8.6$ Hz, 2 H, ArH), 8.17 (d, $J = 8.7$ Hz, 2 H, ArH) ppm. Anal. calcd. for $C_9H_9NO_2S_2$ (227.31): C, 47.56; H, 3.99; N, 6.16; S, 28.21%. Found: C, 47.30; H, 3.90; N, 6.00; S, 28.00.

2-Cinamaldehyde-1,3-dithiane (3q)[17]

IR (neat): 3083, 3057, 3028, 2963, 2924, 1599, 1576, 1497, 1447, 1434, 1421, 968, 763, 687 cm^{-1}. ^{1}H NMR: $\delta = 3.24$–3.37 (m, 4 H), 5.21 (d, $J = 9.1$ Hz, 1 H), 6.16–6.25 (dd, $J = 9.1$, 15.5 Hz, 1 H), 6.49 (d, $J = 15.5$ Hz, 1 H), 7.22–7.38 (m, 5 H). ^{13}C NMR: $\delta = 39.59$ (2 CH_2), 54.47, 126.60, 127.81, 128.53, 129.02, 130.14, 136.04.

2-Hexyl-1,3-dithiane (3r)[14]

Colorless liquid; IR (neat): 2960, 2929, 2852, 1465, 1429, 1383, 1275, 1102, 979, 855, 728 cm^{-1}. ^{1}H NMR: $\delta = 0.85$ (t, $J = 6.6$ Hz, 3 H, CH_3), 1.25–1.42 (m, 8 H, CH_2), 1.76–1.82 (m, 2 H, CH_2CHS), 3.14–3.25 (m, 4 H, $2 \times SCH_2$), 4.44 (t, $J = 7.08$ Hz, 1 H, SCHS) ppm. Anal. calcd. for $C_9H_{18}S_2$ (190.37): C, 56.78; H, 9.53; S, 33.69%. Found: C, 56.50; H, 9.50; S, 33.50.

2-(4′-(*tert*-Butyldiphenylsilyloxy)butane)-1,3-dithiane (3s)[30]

Colorless liquid; IR (neat): 3068, 2935, 2863, 1588, 1434, 1260, 1107, 835, 748, 707. ^{1}H NMR: $\delta = 1.04$ [s, 9 H, $SiC(CH_3)_3$], 1.57–1.59 (m, 2 H, CH_2), 1.75–1.79 (m, 3 H, CH_2 and $SCH_2CH_aH_bCH_2S$), 1.83–1.93 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.58–2.69 (m, 4 H, SCH_2 and CH_2), 2.71–2.83 (m, 2 H, SCH_2), 3.65 (t, $J = 5.8$ Hz, 2 H, OCH_2), 4.00 (t, $J = 7.1$ Hz, 1 H, CH), 7.34–7.42 (m, 5 H, ArH), 7.64–7.67 (m, 5 H, ArH) ppm. Anal. calcd. for $C_{24}H_{34}OS_2Si$ (430.75): C, 66.92; H, 7.96; S, 14.89%. Found: C, 66.80; H, 7.80; S, 15.00%.

2-(4′-Methoxyphenyl)-1,3-dithiolane (3t)[30]

White solid; mp 65 °C; IR (KBr): 1608, 1520, 1256, 1180, 1028 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.28$–3.35 (m, 2 H, SCH_2), 3.44–3.51 (m, 2 H, SCH_2), 3.77 (s, 3 H, OCH_3), 5.62 (S, 1 H, ArCH), 6.83 (d, $J = 8.56$ Hz, 2 H, ArH), 7.44 (d, $J = 8.76$ Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 40.02$ (2 C), 55.19, 55.94, 113.74 (2 C), 129.04 (2 C), 131.69, 159.25 ppm. Anal. calcd. for $C_{10}H_{12}OS_2$ (212.33): C, 56.57; H, 5.70; S, 30.20. Found: C, 56.70; H, 5.58; S, 30.35.

2-(4′-Methylphenyl)-1,3-dithiane (3u)

IR (neat): 3004, 1510, 1437, 1411, 1277, 1177, 1165, 830, 777 cm^{-1}. ^{1}H NMR: $\delta = 2.32$ (s, 3 H), 3.29–3.52 (m, 4 H), 5.62 (s, 1 H), 7.10 (d, $J = 6.5$ Hz, 2 H), 7.40 (d, $J = 6.5$ Hz, 2 H). ^{13}C NMR: $\delta = 21.11$, 40.20 (2 CH_2), 56.12, 127.80, 129.15, 137.10, 137.84.

2-[4′-Hydroxyphenyl)-1,3-dithiane (3v)[17]

IR (neat): 3188 (br), 2919, 1595, 1509, 1448, 1237, 1173, 838 cm^{-1}. ^{1}H NMR: $\delta = 3.30$–3.51 (m, 4 H), 5.00 (s, 1 H), 5.62 (s, 1 H), 6.73–6.79 (m, 2 H), 7.37–7.43 (m, 2 H). ^{13}C NMR: 40.20 (2 CH_2), 56.01, 115.31, 129.41, 131.99, 155.31.

2-(4′-Hydroxy-3-methoxyphenyl)-1,3-dithiane (3w)

IR (thin film): 3434 (br), 2996, 2918, 1607, 1596, 1509, 1464, 1449, 1427, 1266, 1227, 1145, 1118, 1026 cm^{-1}. ^{1}H NMR: $\delta = 3.29$–3.53 (m, 4 H), 3.88 (s, 3 H), 5.69 (s, 1 H), 6.81 (d, $J = 8.1$ Hz, 1 H), 6.90–7.00 (dd, $J = 8.1$, 1.69 Hz, 1 H), 7.09 (s, 1 H). ^{13}C NMR: $\delta = 40.14$ (2 CH_2), 55.91, 56.69, 110.26, 113.97, 121.07, 131.22, 145.54, 146.47.

2-(4′-*N,N*-dimethylphenyl)-1,3-dithiane (3x)[31]

IR (neat): 757, 824, 949, 1069, 1171, 1230, 1247, 1359, 1443, 1482, 1523, 1609, 2807, 2904, 3054 cm^{-1}. ^1H NMR: $\delta = 2.95$ (s, 6 H), 3.32–3.36 (m, 2 H), 3.48–3.54 (m, 2 H), 5.65 (s, 1 H), 6.81 (d, $J = 6.8$ Hz, 2 H), 7.42 (d, $J = 6.8$ Hz, 2 H). ^{13}C NMR: $\delta = 40.09$ (2 CH_3), 40.80 (2 CH_2), 56.40, 112.60, 125.90, 128.77, 149.88.

2-(3-Formyl)-1,3-dithiane (3y)[32]

IR (neat): 2955, 2926, 2854, 1735, 1465, 1377, 1275, 851, 725 cm^{-1}. ^1H NMR: $\delta = 0.87$ (t, $J = 7.2$ Hz, 3 H), 1.1–1.47 (m, 8 H), 1.79 (br s, 2 H), 3.18 (br s, 4 H), 4.35–4.45 (m, 1 H). ^{13}C NMR: $\delta = 14.07$, 22.57, 28.89, 29.10, 31.47, 38.34 (2 CH_2), 39.41, 53.81.

2-(2′,4′-Dimethoxyphenyl)-1,3-dithiane (3z)

White solid; mp 103 °C; IR (KBr): 2996, 2939, 2893, 2837, 1618, 1505, 1454, 1424, 1326, 1290, 1116, 1039, 992 cm^{-1}. ^1H NMR: $\delta = 1.85$–1.92 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.12–2.17 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.84–2.90 (m, 2 H, SCH_2), 3.05–3.16 (m, 2 H, SCH_2), 3.78 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 5.61 (S, 1 H, ArCH), 6.42 (d, $J = 2.4$ Hz, 1 H, ArH), 6.48 (dd, $J = 2.4$, $J = 8.5$ Hz, 1 H, ArH), 7.48 (d, $J = 8.5$ Hz, Hz, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.20$, 32.41 (2 C), 43.10, 55.30, 55.60, 98.50, 104.70, 119.80, 129.70, 156.40, 160.60 ppm. $C_{12}H_{16}O_2S_2$. Anal. calcd. for $C_{12}H_{16}O_2S_2$ (257.05): C, 56.22; H, 6.29; S, 25.01. Found: C, 56.40; H, 6.10; S, 25.30.

2-Methyl-2-phenyl-1,3-dithiolane (5a)[30]

Gummy liquid; IR (neat): 2971, 2935, 1598, 1491, 1445, 1276, 1071, 1030, 774, 702 cm^{-1}. ^1H NMR: $\delta = 2.14$ (s, 3 H, CH_3), 3.31–3.47 (m, 4 H, $2 \times SCH_2$), 7.19–7.23 (m, 1 H, ArH), 7.28–7.32 (m, 2 H, ArH); 7.72–7.75 (m, 2 H, ArH) ppm. ^{13}C NMR: $\delta = 33.81$, 40.22 (2 C), 68.52, 126.68 (2 C), 126.99, 127.90 (2 C), 145.82 ppm. Anal. calcd. for $C_{10}H_{12}S_2$ (196.34): C, 61.17; H, 6.16; S, 32.66. Found: C, 61.01; H, 6.09; S, 32.43.

2-Methyl-2-tolyl-1,3-dithiane (5b)

IR (neat): 731, 819, 1018, 1072, 1126, 1185, 1275, 1371, 1443, 1508, 1610, 1654, 2861, 2921, 2965, 3022 cm^{-1}. ^1H NMR: $\delta = 2.14$ (s, 3 H), 2.32

(s, 3 H), 3.30–3.52 (m, 4 H), 7.11 (d, $J = 8$ Hz, 2 H), 7.63 (d, $J = 8$ Hz, 2 H). ^{13}C NMR: $\delta = 20.89$, 33.87, 40.29 (2 CH_2), 68.39, 126.67, 128.64, 136.74, 142.87.

2-Phenyl-2-tolyl-1,3-dithiane (5c)[33]

IR (thin film): 696, 741, 1032, 1186, 1275, 1443, 1506, 1594, 2874, 2921, 3022, 3056 cm^{-1}. ^{1}H NMR: $\delta = 2.31$ (s, 3 H), 3.39 (m, 4 H), 7.08 (d, $J = 8.1$ Hz, 2 H), 7.23–7.27 (m, 3 H), 7.48 (d, $J = 8$ Hz, 2 H), 7.60 (m, 2 H). ^{13}C NMR: $\delta = 20.96$, 40.12 (2 CH_2), 127.10, 127.73, 127.97, 128.17, 128.64, 136.95, 141.47, 144.77.

2-Methyl-2-(4-hydoxyphenyl)-1,3-dithiane (5d)[30]

IR (neat): 687, 738, 831, 844, 1074, 1180, 1230, 1273, 1375, 1442, 1508, 1596, 1608, 2876, 2929, 2969, 3225 (br) cm^{-1}. ^{1}H NMR: $\delta = 2.13$ (s, 3 H), 3.35–3.51 (m, 4 H), 5.60 (br s, 1 H), 6.75 (d, $J = 7.7$ Hz, 2 H), 7.63 (d, $J = 7.7$ Hz, 2 H). ^{13}C NMR: $\delta = 33.91$, 40.35 (2 CH_2), 68.22, 114.71, 128.33, 137.73, 154.64.

2-Methyl-2-(4-chlorophenyl)-1,3-dithiane (5e)[34]

IR (neat): 734, 830, 1011, 1069, 1093, 1275, 1372, 1396, 1422, 1444, 1489, 1570, 1591, 2860, 2922, 2966, 3059 cm^{-1}. ^{1}H NMR: $\delta = 2.1$ (s, 3 H), 3.30–3.45 (m, 4 H), 7.26 (d, $J = 6.4$ Hz, 2 H), 7.68 (d, $J = 6.4$ Hz, 2 H). ^{13}C NMR: $\delta = 33.46$, 40.31 (2 CH_2), 67.82, 127.87, 128.24, 132.70, 144.55.

2-Benzyl-2-methyl-[1,3]dithiolane (5f)[34]

Bp 129–130/1.5 °C. IR (neat): 3083, 3060, 3027, 2959, 2919, 2856, 1602, 1494, 1452,1372, 1276, 1083, 752, 698 cm^{-1}. ^{1}H NMR: $\delta = 1.71$ (s, 3 H), 3.00–3.32 (m, 6 H), 7.15–7.36 (m, 5 H). ^{13}C NMR: d = 31.78, 39.72 (2 CH2), 51.41, 66.59, 126.68, 127.66, 130.69, 137.74.

2,2-Diphenyl-[1,3]dithiolane (5g)

Mp 105–106 °C. IR (thin film): 696, 741, 1032, 1186, 1275, 1443, 1506, 1594, 2874, 2921, 3022, 3056 cm^{-1}. ^{1}H NMR: $\delta = 3.39$ (m, 4 H), 7.08 (d, $J = 8.1$ Hz, 4 H), 7.23–7.27 (m, 6 H). ^{13}C NMR: $\delta = 40.12$ (2 CH2), 127.10, 127.73, 127.97, 128.17, 128.64, 136.95, 141.47, 144.7.

2-Methyl-2-(4-bromophenyl)-1,3-dithiolane (5h)[35]

IR (neat): 731, 827, 1007, 1077, 1275, 1391, 1486, 1583, 2858, 2922, 2965, 3061 cm^{-1}. ^1H NMR: $\delta = 2.07$ (s, 3 H), 3.30–3.45 (m, 4 H), 7.38 (d, $J = 6.8$ Hz, 2 H), 7.60 (d, $J = 6.8$ Hz, 2 H). ^{13}C NMR: $\delta = 34.10$, 41.01 (2 CH_2), 68.50, 114.03, 129.60, 131.50, 145.76.

1,4-Dithiaspiro(4.4)nonane (5i)[35]

Colorless liquid; IR (neat): 2960, 2924, 2878, 1449, 1275, 1168, 1101, 978, 851, 692 cm^{-1}. ^1H NMR: $\delta = 1.74$–1.77 (m, 4 H, CH_2), 2.07–2.14 (m, 4 H, CH_2), 3.30 (s, 4 H, $2 \times SCH_2$) ppm. ^{13}C NMR: $\delta = 24.48$ (2 C), 39.37 (2 C), 43.92 (2 C), 70.86 ppm. Anal. calcd. for $C_7H_{12}S_2$ (160.30): C, 52.45; H, 7.55; S, 40.00. Found: C, 52.12; H, 7.50; S, 39.85.

2-Ethyl-2-pentyl-1,3-dithiolane (5j)[35]

Colorless liquid; IR (neat): 2960, 2930, 2853, 1465, 1373, 1276, 1148, 984, 892, 851, 810, 733, 692 cm^{-1}. ^1H NMR: $\delta = 0.85$ (t, $J = 7.0$ Hz, 3 H, CH_3), 0.99 (t, $J = 7.30$ Hz, 3 H, CH_3), 1.21–1.31 (m, 4 H, CH_2), 1.38–1.46 (m, 2 H, CH_2), 1.84–1.93 (m, 4 H, CH_2), 3.21 (br. s, 4 H, SCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.16$, 14.01, 22.53, 26.58, 31.95, 36.12, 39.37 (2 C), 42.88, 72.41 ppm. Anal. calcd. for $C_{10}H_{20}S_2$ (204.40): C, 58.76; H, 9.86; S, 31.38. Found: C, 58.54; H, 9.79; S, 31.09.

1,4-Dithiaspiro(4.6)undecane (5k)[36]

While solid; mp 56 °C; SiO_2–TLC (hexane). IR (KBr): 2919, 2842, 1460, 1424, 1275, 1244, 1234, 1152, 1101, 963, 846, 692 cm^{-1}. ^1H NMR: $\delta = 1.57$ (m, 8 H, CH_2), 2.17–2.19 (m, 4 H, CH_2), 3.26 (s, 4 H, SCH_2) ppm. ^{13}C NMR: $\delta = 25.62$ (2 C), 28.55 (2 C), 38.84 (2 C), 46.11 (2 C), 71.88 ppm. Anal. calcd. for $C_9H_{16}S_2$ (188.36): C, 57.39; H, 8.56; S, 34.05. Found: C, 57.18; H, 8.48; S, 33.87.

1,4-Dithiaspiro(5.5)decane (5l) [35]

Colorless liquid; IR (neat): 2930, 2853, 1440, 1265, 1127, 1015, 907, 861, 764 cm^{-1}. ^1H NMR: $\delta = 1.43$–1.49 (m, 2 H, CH_2), 1.60–1.67 (m, 4 H, CH_2), 1.96–2.02 (m, 6 H, $SCH_2CH_2CH_2S$ and $2 \times CH_2$), 2.79–2.83 (m, 4 H, $2 \times SCH_2$) ppm. ^{13}C NMR: $\delta = 21.97$ (2 C), 25.79 (2 C), 25.87, 26.12, 37.86 (2 C), 50.32 ppm. Anal. calcd. for $C_9H_{16}S_2$ (188.36): C, 57.39; H, 8.56; S, 34.05. Found: C, 57.14; H, 8.50; S, 34.23.

2-Butyl-2-methyl-1,3-dithiolane (5m)[35]

IR (neat): 686, 733, 852, 972, 1056, 1139, 1276, 1374, 1448, 2859, 2927, 2957 cm^{-1}. ^1H NMR: $\delta = 0.92$ (t, $J = 7.1$ Hz, 3 H), 1.30–1.38 (m, 2 H), 1.43–1.54 (m, 2 H), 1.75 (s, 3 H), 1.90–1.95 (m, 2 H), 3.30 (m, 4 H). ^{13}C NMR: $\delta = 14.00$, 22.90, 29.50, 32.30, 40.00 (2 CH_2), 45.80, 66.80.

2, 2-Dipropyl-1,3-dithiolane (5n)[36]

IR (neat): 2961, 2873, 1707, 1459, 1380, 1275 cm^{-1}. ^1H NMR: $\delta = 0.90$ (t, $J = 7.3$ Hz, 6 H), 1.35–1.63 (m, 4 H), 2.73–2.76 (m, 1 H), 3.13–3.23 (m, 4 H), 4.63 (d, $J = 6.2$ Hz, 1 H). ^{13}C NMR: $\delta = 10.91$ (2 CH_3), 23.94 (2 CH_2), 28.72, 38.42 (2 CH_2), 58.22.

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