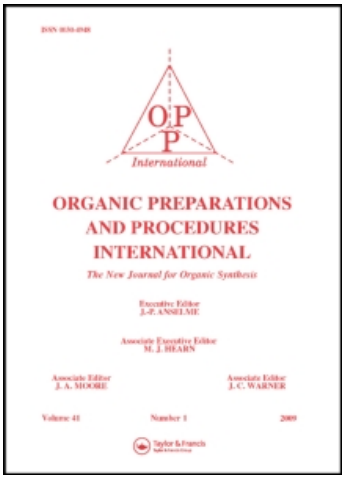

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AN EFFICIENT METHOD FOR THE THIOACETALIZATION OF CARBONYL COMPOUNDS IN THE PRESENCE OF CATALYTIC AMOUNTS OF BENZYLTRIPHENYLPHOSPHONIUM TRIBROMIDE

A. R. Hajipour[ab]; S. A. Pourmousavi[a]; A. E. Ruoho[b]
[a] Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, IRAN [b] Department of Pharmacology, University of Wisconsin Medical School, Madison, WI, USA

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AN EFFICIENT METHOD FOR THE THIOACETALIZATION OF CARBONYL COMPOUNDS IN THE PRESENCE OF CATALYTIC AMOUNTS OF BENZYLTRIPHENYLPHOSPHONIUM TRIBROMIDE

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A. R. Hajipour,*[†,††] S. A. Pourmousavi[†] and A. E. Ruoho[††]

[†] *Pharmaceutical Research Laboratory, Department of Chemistry Isfahan University of Technology, Isfahan 84156, IRAN*

[††] *Department of Pharmacology, University of Wisconsin Medical School 1300 University Avenue, Madison, WI, USA 53706-1532*

Email: haji@cc.iut.ac.ir

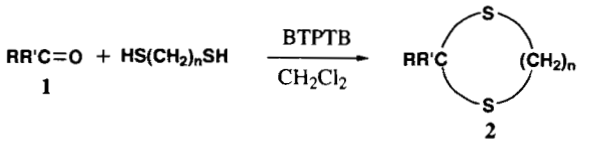
The protection of carbonyl groups is often necessary in multi-step syntheses. Among carbonyl protecting groups, dithioacetals constitute an important class of compounds as acyl anion equivalents[1] or masked methylene functions in carbon-carbon bond forming reactions. They are versatile[2] due to their straightforward preparation and also to their stability under basic or mildly acidic conditions. Although several methods have been reported for protection of carbonyl compounds as dithioacetals,[3-17] many of these procedures have certain limitations such as low yields, harsh reaction conditions, long reaction times and expensive reagents. Therefore milder, simpler and more efficient alternatives are still desirable for protection of carbonyl compounds. Organoammonium tribromide[18] are extremely useful reagents in organic synthesis particularly for the deprotection of dithioacetals and of TBDMS ethers,[19,20] and protection/deprotection of THP ethers and in natural product synthesis.[21,22] Several tribromides have been reported,[23] but their preparation involves mostly the use of elemental bromine[24] which causes an environmental problem.[25] As part of our studies to develop new methods for organic transfomations,[26-30] we report a new and environmentally benign method for the synthesis of benzyltriphenylphosphonium tribromide (**BTPTB**) and its applications as a mild and efficient catalyst for the protection of carbonyl groups as dithioacetals.

The reagent was synthesized by the dropwise addition of an aqueous solution of 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 quantitative yields of a yellow precipitate that showed an intense electronic absorbtion at 279 nm typical of the tribromide.[18] Reagent **1** is easily handled, very stable and can be stored at the bench for months without losing its activity. This reagent is an efficient catalyst for conversion of carbonyl compounds to the corresponding dithioacetals in dichloromethane and also is a highly chemoselective catalyst for the conversion of aldehydes in the presence of ketones to the corresponding dithioacetals

Initially we investigated the protection of aldehydes **1** to the corresponding dithioacetals **2** and **3** with 1,2-ethanedithiol, 1,3-propanedithiol or ethylthiol in dichloromethane in the presence of 5 mol% of benzyltriphenylphosphonium tribromide (**BTPTB**) (*Table 1*). This

reaction gave dithioacetal derivatives of aldehyde in 85-98% yield after 3-25 min. The reaction was used with a wide variety of aldehydes containing electron-withdrawing and electron-donating substituents. The protection of heteroaromatic and α,β-unsaturated aldehydes also were carried out under similar reaction conditions (*Table 1*). The reaction proceeded efficiently at ambient temperature under essentially nearly neutral conditions. Protection of acid sensitive substrates such as furfural as its dithioacetal derivative proceeded in a nearly quantitative yield without the formation of any side-products. In addition, no bromination occurred at the double bond or α position of the C=O group of aldehydes or ketones. Bromination of the aromatic ring of aldehydes or ketones under this condition did not occur at all.

In comparison to aldehydes the reaction of ketones **1** with 1,2-ethanedithiol in CH_2Cl_2 in the presence of 5 mol% of **BTPTB** required longer reaction times (10-15 h) to afford the corresponding thioacetals **2** (*Table 1*).



a) R = C_6H_5, R^1 = H, n = 2; b) R = C_6H_5, R^1 = H, n = 3; c) R = 4-(Cl)C_6H_4, R^1 = H, n = 2; d) R = 2-(MeO)C_6H_4, R^1 = H, n = 2; e) R = 3-(MeO)C_6H_4, R^1 = H, n = 3; f) R = 4-(TBSO)C_6H_4, R1 = H, n = 3; g) R = 4-(Allylo)C_6H_4, R^1 = H, n = 3; h) R = 4-(Cyclohexyl)C_6H_4, R^1 = H, n = 3; i) R = 4-(BzO)C_6H_4, R^1 = H, n = 3; j) R = $C_6H_5CH_2$, R^1 = H, n = 3; k) R = 4-(OH)C_6H_4, R^1 = H, n = 3; l) R = 2-Furyl, R^1 = H, n = 3; m) R = 4-(NO_2)C_6H_4, R^1 = H, n = 2; n) R = C_6H_5CH=CH, R^1 = H, n = 3; o) R = n-C_6H_{13}, R^1 = H, n = 2; p) R = TBDPSO$CH_2(CH_2)_3$, R^1 = H, n = 3; q) R = 4-(MeO)C_6H_4, R^1 = H, n = 2; r) R = 4-(Me)C_6H_4, R^1 = H, n = 2; s) R = 4-(OH)C_6H_4, R^1 = H, n = 2; t) R = 4-(Me_2N)C_6H_4, R^1 = H, n = 2; u) R = $CH_3(CH_2)_4$, R^1 = H, n = 2; v) R = 2,5-(MeO)2C_6H_4, R^1 = H, n = 2; x) R = C_6H_5, R^1 = Me, n = 2; y) R = 4(Me)C_6H_4, R^1 = H, n = 2; z) R = 4-(Me)C_6H_4, R^1 = C_6H_5, n = 2; a') R = 4-(OH)C_6H_4, R^1 = Me, n = 2; b') R = 4–(Cl)C_6H_4, R^1 = Me, n = 2; c') R = C6H_5CH_2, R^1 = Me, n = 2; d') R = C_6H_5, R^1 = C_6H_5, n = 3; e') R = 4-(Br)C_6H_4, R^1 = Me, n = 2; f') R, R^1 = -$(CH_2)_4$-, n = 2; g') R = $CH_3(CH_2)_4$, R^1 = CH_3CH_2, n = 2; h') R, R^1 = -$(CH_2)_6$-, n = 2; i') R, R^1 = -$(CH_2)_5$-, n = 2; j') R = $CH_3(CH_2)_4$, R^1 = Me, n = 2; k') R = $CH_3(CH_2)_2$, R^1 = $CH_3(CH_2)_2$, n = 2

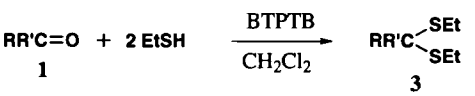
Table 1. Thioacetalization of Aldehyde and Ketones with Reagent 1[a]

Cmpd	Yield (%)	Time	mp (°C) (bp /mm)[b]	*lit.*	Elemental Analysis (Found) C	H	N	S
2a	95	15 min	(166-167/20)	(145/1)[31]	----	----	----	
2b	90	10 min	74-75	74[20]	----	----	----	
2c	95	7 min	59-61	60-62[20]	----	----	----	
2d	95	10 min	64-65	62.5-63.5[32]	----	----	----	
2e	98	10 min	65-67	65[32]	----	----	----	
2f	95	10 min	semi solid	----	57.64 (57.60)	7.74 (7.70)	----	20.51 (20.42)
2g	90	7 min	81-82	81[20]	----	----	----	
2h	92	15 min	103-104	103-104[20]	----	----	----	

Table 1. Continued...

Cmpd	Yield (%)	Time	mp (°C) (bp /mm)[b]	*lit.*	Elemental Analysis (Found) C	H	N	S
2i	98	5 min	164-165	163-164[20]	----	----	----	
2j	93	3 min	(133-138/2)	(112-115/0.25)[20]	----	----	----	
2k	95	5 min	157-159	158[20]	----	----	----	
2l	98	8 min	41-43	(42[20]	----	----	----	
2m	90	20 min	75-76	----	47.56 (47.30)	3.99 (3.90)	6.16 (6.00)	28.21 (28.00)
2n	85	10 min	62-63	63-64[15]	----	----	----	
2o	85	10 min	49-50	(49-50[33]	----	----	----	
2p	87	8 min	semi solid	----	66.92 (66.80)	7.96 (7.80)	----	14.89 (15.00)
2q	98	10 min	64-65	65[20]	----	----	----	
2r	90	7 min	58-59	56-58 [15]	----	----	----	
2s	92	15 min	119-120	116[34]	----	----	----	
2t	85	15 min	106-107	107[34]	----	----	----	
2u	90	12 min	(120-122/16)	----	54.49 (54.40)	9.15 (9.22)	----	36.26 (36.2)
2v	90	12 min	102-103	102[20]	----	----	----	
2x	90	10 h	34-36	35[35]	----	----	----	
2y	95	10 h	(94-95/0.6)	(141/11.3)[36]	----	----	----	
2z	90	15 h	52-53	----	70.54 (70.49)	5.91 (5.96)	----	23.54 (23.60)
2a'	85	15 h	81-82	80-81[34]	----	----	----	
2b'	85	10 h	(202/30)	----	52.05 (51.95)	4.80 (4.90)	----	27.79 (27.68)
2c'	91	10 h	(129-130/1.5)	(108/0.7)[37]	----	----	----	
2d'	88	14 h	105-106	105[34]	----	----	----	
2e'	87	12 h	(162-163/11)	----	43.64 (43.58)	4.03 (4.11)	----	23.30 (23.22)
2f'	89	8 h	(89/5)	(107/15)[38]	----	----	----	
2g'	91	9 h	(92-93/12)	----	58.77 (58.60)	9.86 (9.98	----	31.37 (31.42)
2h'	85	8 h	54-55	54[39]	----	----	----	
2i'	87	10 h	(107/15)	(53-55/1.5)[39]	----	----	----	
2j'	90	7 h	(72-73/12)	(65-66/8.5)[39]	----	----	----	
2k'	90	7 h	(95/5)	(86/2)[40]	----	----	----	
3a	98	7 min	(173-176/1)	----	51.34 (51.55)	5.87 (5.93)	5.44 (5.31)	24.91 (24.74)
3b	85	25 min	43-44	43[20]	----	----	----	
3c	90	20 min	light yellow oil	----	61.13 (61.04)	8.29 (8.36)	5.48 (5.56)	25.10 (25.07)

In CH_2Cl_2 at RT. Identity of products confirmed by comparison with authentic samples (TLC, GC, IR and ^{1}HNMR). b) bp/pressure mm.



a) 4-$(NO_2)C_6H_4$, R^1 = H; b) 4-$(MeO)C_6H$, R^1 = H; c) 4-$(Me_2N)C_6H_4$, R^1 = H

Table 2. ^{1}H NMR and ^{13}C NMR of Compounds **2** and **3**

Cmpd	^{1}H NMR (δ)	^{13}C NMR (δ)
2a	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)	40.81, 56.82, 128.52, 128.56, 129.02, 140.94
2b	1.85-1.96 (m, 1 H), 2.09-2.16 (m, 1 H), 2.85-2.90 (m, 2 H, SCH_2), 2.99-3.07 (m, 2 H), 5.16 (S, 1 H), 7.24-7.35 (m, 3 H), 7.45-7.47 (m, 2 H)	24.96, 31.95, 51.34, 127.61, 128.29, 128.59, 138.99
2c	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)	40.27, 55.44, 128.57, 129.30, 133.61, 139.02
2d	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)	40.04, 55.08, 56.04, 113.34, 120.14, 129.32, 141.91, 159.45
2e	3.25-3.53 (m, 4 H), 3.73 (s, 3 H), 5.54 (s, 1 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)	40.24, 56.35, 101.20, 107.73, 108.32, 121.35, 133.88, 147.46, 147.85
2f	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 = 8.5Hz, 2 H), 7.38 (d, J = 8.5Hz, 2 H)	14.2, 19.5, 27.6, 40.5, 57.3, 120.8, 131.7, 134.5, 156.3
2g	1.84-1.97 (m, 1 H), 2.11-2.17 (m, 1 H), 2.86-2.91 (m, 2 H), 3.00-3.14 (m, 2 H), 4.50-4.52 (m, 2 H), 5.13 (s, 1 H), 5.27 (dd, J = 3.0, 10.6 Hz, 1 H), 5.39 (dd, J = 3.2, J = 17.1 Hz, 1 H), 5.98-6.08 (m), 6.87 (d, J = 8.8 Hz, 2 H), 7.38 (d, J = 8.8 Hz, 2 H)	24.97, 32.10, 50.66, 68.81, 114.86, 118.26, 128.86, 131.34, 133.03, 158.49
2h	1.57-1.65 (m, 2 H), 1.76-1.89 (m, 2 H), 1.91-2.03 (m, 1 H), 2.05-2.18 (m, 3 H), 2.84-2.92 (m, 2 H), 3.01_3.15 (m, 2 H,), 3.54-3.55 (m, 1 H), 5.10 (s, 1 H), 5.81 (dd, J = 2.0, 10.0 Hz, 1 H), 6.03-6.08 (m, 1 H), 6.87(d, J = 8.8 Hz, 2 H), 7.37 (d, J = 8.8 Hz, 2 H)	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, 1 31.18 (2 C), 154.14 ppm
2i	1.88-1.98 (m, 1 H), 2.15-2.18 (m, 1 H), 2.89-2.93 (m, 2 H), 3.03-3.09 (m, 2 H,), 5.20 (S, 1 H), 7.20 (d, J = 8.8 Hz, 2 H), 7.51 (m, 2 H), 7.53 (d, J = 8.5Hz, 2 H), 7.63 (m, 1 H), 8.18 (m, 2 H)	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 pp
2j	3.04 (d, J = 7.1 Hz, 2 H), 3.10-3.21 (m, 4 H), 4.66 (t, J = 7.1 Hz, 1 H), 7.16-7.26 (m, 5 H)	31.72, 36.52, 44.22, 52.54, 125.52, 127.52, 128.61, 140.19
2k	1.85-1.96 (m, 1 H), 2.12-2.19 (m, 1 H), 2.86-2.92 (m, 2 H), 3.01-3.08 (m, 2 H), 5.12 (S, 1 H), 6.77 (d, J = 8.2 Hz, 2 H), 7.31 (d, J = 8.3 Hz, 2 H)	25.06, 32.18 (2 C), 50.74, 115.58 (2 C), 129.18 (2 C), 131.45, 155.61
2l	1.92-2.01 (m, 1 H), 2.08-2.16 (m, 1 H), 2.88-2.93 (m, 4 H), 5.20 (s, 1 H), 6.32 (dd, J = 2.0, J = 3.2 Hz, 1 H), 6.37 (d, J = 3.1 Hz, 1 H), 7.34 (d, J = 1.9 Hz, 1 H)	25.22, 30.24 (2 C), 41.99, 107.83, 110.56, 142.27, 151.66
2m	3.37-3.43 (m, 2 H), 3.45-3.55 (m, 2 H), 5.65 (s, 1 H), 7.66 (d, J = 8.6 Hz, 2 H), 8.17 (d, J = 8.7 Hz, 2 H)	36.92, 57.63, 123.49, 129.82, 144.39, 148.78
2n	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)	39.59 (2 CH_2), 54.47, 126.60, 127.81, 128.53, 129.02, 130.14, 136.04
2o	0.85 (t, J = 6.6 Hz, 3 H), 1.25-1.42 (m, 8 H), 1.76-1.82 (m, 2 H), 3.14-3.25 (m, 4 H, 2), 4.44 (t, J = 7.08 Hz, 1 H)	13.98, 23.12, 25.88, 28.96, 32.53, 33.42, 37.36, 54.37

Table 2. Continued...

Cmpd	^{1}H NMR (δ)	^{13}C NMR (δ)
2p	^{1}H NMR: δ = 1.04 (s, 9 H), 1.57-1.59 (m, 2 H), 1.75-1.79 (m, 3 H), 1.83-1.93 (m, 1 H), 2.58-2.69 (m, 4), 2.71-2.83 (m, 2 H), 3.65 (t, J = 5.8 Hz, 2 H), 4.00 (t, J = 7.1 Hz, 1), 7.34-7.42 (m, 5 H), 7.64-7.67 (m, 5 H)	14.47, 20.52, 29.78, 31.72, 34.68, 36.50, 38.49, 50.40, 128.12, 129.79, 133.04, 135.84
2q	^{1}H NMR: δ = 3.28-3.35 (m, 2 H), 3.44-3.51 (m, 2 H), 3.77 (s, 3 H), 5.62 (S, 1 H), 6.83 (d, J = 8.56Hz, 2 H), 7.44 (d, J = 8.76 Hz, 2 H)	40.02 (2 C), 55.19, 55.94, 113.74 (2 C), 129.04 (2 C), 131.69, 159.25
2r	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)	21.11, 40.20, 56.12, 127.80, 129.15, 137.10, 137.84
2s	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)	40.20 (2 CH_2), 56.01, 115.31, 129.41, 131.99, 155.31
2t	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 = 6.8Hz, 2 H), 7.42 (d, J = 6.8Hz, 2 H)	40.09, 40.80, 56.40, 112.60, 125.90, 128.77, 149.88
2u	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)	14.07, 22.57, 28.89, 29.10, 31.47, 38.34, 39.41, 53.81
2v	1.85-1.92 (m, 1 H), 2.12-2.17 (m, 1 H), 2.84-2.90 (m, 2 H), 3.05-3.16 (m, 2 H), 3.78 (s, 3 H), 3.83 (s, 3 H,), 5.61 (S, 1 H), 6.42 (d, J = 2.4 Hz, 1 H), 6.48 (dd, J = 2.4, J = 8.5Hz, 1 H), 7.48 (d, J = 8.5 Hz, 1 H)	25.20, 32.41 (2 C), 43.10, 55.30, 55.60, 98.50, 104.70, 119.80, 129.70, 156.40, 160.60
2x	2.14 (s, 3 H), 3.31-3.47 (m, 4 H), 7.19-7.23 (m, 1 H), 7.28-7.32 (m, 2 H); 7.72-7.75 (m, 2 H)	33.81, 40.22, 68.52, 126.68, 126.99, 127.90 , 145.82
2y	δ = 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)	20.89, 33.87, 40.29 (2 CH_2), 68.39, 126.67, 128.64, 136.74, 142.87
2z	2.31 (s, 3 H), 3.39 (m, 4 H), 7.08 (d, *J* = 8.1Hz, 2 H), 7.23-7.27 (m, 3 H), 7.48 (d, *J* = 8Hz, 2 H), 7.60 (m, 2 H)	20.96, 40.12 (2 CH_2), 127.10, 127.73, 127.97, 128.17, 128.64, 136.95, 141.47, 144.77
2a'	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)	33.91, 40.35, 68.22, 114.71, 128.33, 137.73, 154.64
2b'	2.1 (s, 3 H), 3.30-3.45 (m, 4 H), 7.26 (d, J = 6.4Hz, 2 H), 7.68 (d, *J* = 6.4 Hz, 2 H)	33.46, 40.31, 67.82, 127.87, 128.24, 132.70, 144.5
2c'	1.71 (s, 3 H), 3.00–3.32 (m, 6 H), 7.15–7.36 (m, 5 H)	31.78, 39.72, 51.41, 66.59, 126.68, 127.66, 130.69, 137.74
2d'	3.39 (m, 4 H), 7.08 (d, J = 8.1 Hz, 4 H),7.23–7.27 (m, 6 H).	40.12, 127.10, 127.73, 127.97, 128.17, 128.64, 136.95, 141.47, 144.77
2e'	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)	34.10, 41.01, 68.50, 114.03, 129.60, 131.50, 145.76
2f'	1.74-1.77 (m, 4 H), 2.07-2.14 (m, 4 H), 3.30 (s, 4 H)	24.48, 39.37, 43.92, 70
2g'	0.85 (t, J = 7.0 Hz, 3 H), 0.99 (t, J = 7.30 Hz, 3 H), 1.21-1.31 (m, 4 H), 1.38-1.46 (m, 2 H), 1.84-1.93 (m, 4 H), 3.21 (br. s, 4 H)	11.16, 14.01, 22.53, 26.58, 31.95, 36.12, 39.37, 42.88, 72.41
2h'	1.57 (m, 8 H), 2.17-2.19 (m, 4 H), 3.26 (s, 4 H)	25.62, 28.55, 38.84, 46.11, 71.88
2i'	1.43-1.49 (m, 2 H), 1.60-1.67 (m, 4 H), 1.96-2.02 (m, 6 H), 2.79-2.83 (m, 4 H)	21.97, 25.79, 25.87, 26.12, 37.86, 50.32
2j'	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)	14.00, 22.90, 29.50, 32.30, 40.00, 45.80, 66.80

Table 2. Continued...

Cmpd	^{1}H NMR (δ)	^{13}C NMR (δ)
2k'	0.87-0.93 (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), 4.62-4.65 (d, J = 6.2 Hz, 1 H).	10.91 (2 CH_3), 23.94 (2 CH_2), 28.72, 38.42 (2 CH_2), 58.22.
3a	1.22 (t, *J* = 7.0 Hz, 6 H), 2.58-2.46 (m, 4 H), 4.92 (s, 1 H), 7.65 (d, *J* = 8.0 Hz, 2 H), 8.20 (d, J = 8.0, 8.0 Hz, 2 H).	15.60, 22.20, 51.11, 123.52, 1 24.45, 129.88, 148.95
3b	1.22 (t, J = 7.3 Hz, 6 H), 2.46-2.63 (m, 4 H, 2), 3.80 (s, 3 H), 4.91 (s, 1 H), 6.85 (d, J = 8.6 Hz, 2 H), 7.37 (d, J = 8.5 Hz, 2 H).	14.24 (2 C), 26.15 (2 C), 51.69, 55.22, 113.75 (2 C), 128.77 (2 C), 132.37, 159.00
3c	1.16 (t, J = 7.0 Hz, 6 H), 2.62-2.43 (m, 4 H), 2.98 (s, 6 H), 4.86 (s, 1 H), 6.68 (d, J = 8.0 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H).	15.60, 22.20, 46.70, 51.11, 113.02, 127.80, 12985, 142.93

This procedure is highly chemoselective, providing protection of an aldehyde in the presence of a ketone. Treatment of one equimolar mixture of benzaldehyde and acetophenone in the presence of 1,3-ethanedithiol (1.4 equimolar) and catalytic amount of reagent (**BTPTB**) (5 mol%) in CH_2Cl_2 at room temperature for 25 min produced only the 1,3-dithiolane derivative of benzaldehyde while the acetophenone was recovered completely. The other competition reaction between *p*-anisaldehyde and veratraldehyde and the corresponding acetophenones gave only 5% of the thioketals. Treatment of 4-acetylbenzaldehyde in the presence of 1,2-ethanedithiol (1.4 equimolar) and catalytic amount of reagent (**BTPTB**) (5 mol%) in CH_2Cl_2 at room temperature for 60 min produced only 1,3-ditholane of the aldehyde group in 92% yields. Reaction of α,β-unsaturated ketones such as 2-cyclohexenone or 4-phenyl-3-butyn-2-one with 1,2-ethanedithiol (1.4 equimolar) and catalytic amount of reagent (**BTPTB**) (5 mol%) in CH_2Cl_2 at room temperature for 24 hr failed. A noteworthy aspect of this reagent is that it is recyclable. To recover the reagent after completion of the reaction and extraction of the product, the residue was dissolved in water and treated with a new batch of Oxone® and NaBr to regenerate the reagent. This method therefore is also important from the point of view of green chemistry.

In summary, we report here an efficient method for the protection of aldehydes and ketones with thiols to form the corresponding dithioacetals in CH_2Cl_2. This procedure is an efficient method for protection of aliphatic and aromatic ketones and aldehydes since the yields of the products are high and the reaction times are low.

EXPERIMENTAL SECTION

All yields refer to isolated products after purification. All of the products were characterized by comparison of their spectral (IR, ^{1}H-NMR, CHN, TLC and GC) and physical data (melting and boiling points) (**Tables 1 and 2**) with those of authentic samples.[20-40] 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 CH_2Cl_2 at room temperature.

Preparation of Benzyltriphenylphosphonium Tribromide.- To a solution of benzyltriphenylphosphonium bromide (0.01 mol, 3.88 g) and sodium bromide (0.023 mol, 2.37 g) in water (100 mL) was added dropwise a solution of Oxone® ($2KHSO_5.KHSO_4.K_2SO_4$) (0.022 mol, 13.65 g) in water (20 mL) under stirring at room temperature until a yellow precipitate was formed. After stirring for 30 min, the solid was collected and washed with water (3 x 30 mL). The filter cake was dried and recrystallized from $CHCl_3$ to afford (**BTPTB**) as yellow crystals (4.15 g, 70% yields), mp: 136-137°C. IR (**KBr**) δ: 3050 (m), 2950 (s), 1580 (s), 1115 (s), 900 (m) cm^{-1} ^{1}HNMR: δ 7.22-7.98 (m, 20H) 4.90 (d, J = 18 Hz, 2H), UV (CH_2Cl_2) λ_{max}: 279 nm.

Anal.- Calcd for $C_{25}H_{22}Br_3P$: C: 50.84, H: 3.72. Found C: 50.74, H: 3.60.

Thioacetalization of Carbonyl Compounds in CH_2Cl_2 at Room Temperature.- To a solution of 1,2-ethanedithiol, 1,3-propanedithiol or ethanethiol (12 mmol) and aldehydes or ketones (10 mmol) in CH_2Cl_2 (10 mL) were added dropwise a solution of (BTPTB) (0.5 mmol 0.3 g) in CH_2Cl_2 (4 mL). The reaction mixture was stirred at room temperature till the TLC or GC showed complete disappearance of starting material, the solvent was evaporated to dryness under reduced pressure and the by-product was precipitated by adding of diethyl ether (3 x 20 mL) and collected. The filtrate was evaporated under reduced pressure and the resulting crude material was purified by column chromatography in silica gel (10 g) (EtOAc:*n*-hexane, 25:75) by gradient mehod to afford the pure dithioacetals (**Table 1**).

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FERRIC CHLORIDE-CATALYZED DEOXYGENATIVE CHLORINATION OF CARBONYL COMPOUNDS TO HALIDES

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Z. Li,[†] C. Sheng,[†] H. Qiu*[†] and Y. Zhang[††]

[†] *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education Hangzhou Teachers College, Hangzhou, 310012, P. R. CHINA*

[††] *Department of Chemistry, Zhejiang University Hangzhou, 310028, P. R. CHINA*

e-mail: huayuqiu@hotmail.com

Deoxygenative chlorination is an important method for the conversion of organic molecules with oxygen functionalities to their chlorides.[1] The reaction of carbonyl compounds with PCl_5, or WCl_6 is a well-known route to vinyl chlorides, *gem*-dichlorides or 1,1,2-trichlorides.[2] However, the direct conversion of carbonyl compounds into organic halides has been largely unexplored. Recently, Baba and coworkers[3] reported that $In(OH)_3$ was an effective catalyst for the deoxygenative halogenation of aromatic aldehydes or ketones in good yields by using chlorodimethylsilane in chloroform, but that this method failed with aliphatic aldehydes. Furthermore, the use of chlorinated solvent does not meet the increasing requirement of a friendly environment. Thus more economical catalysts and new eco-friendly solvents are desirable. Herein we report the $FeCl_3$ catalyzed deoxygenative chlorination of aldehydes and ketones with dichloromethylsilane.