Montmorillonite impregnated with $Bi(NO_3)_3$ as an efficient catalyst for the thioacetalisation of carbonyl compounds in the solid state

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Abstract

Montmorillonite impregnated with $Bi(NO_3)_3$ efficiently and chemoselectively catalyzes the thioacetalisation of both aliphatic and aromatic carbonyl compounds under solvent free conditions. The sterically hindered ketones are also catalyzed in excellent yields. This methodology involves mild reaction conditions, good yields and it is economically cheaper and compatible

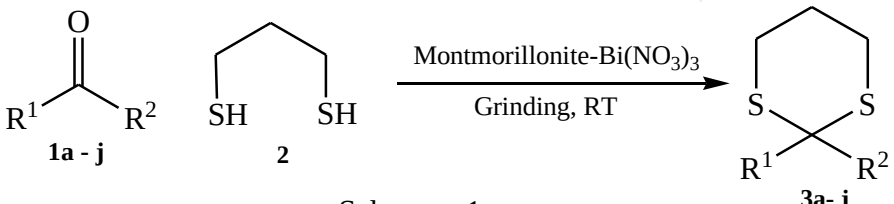
Index Terms: Thioacetalisation, Montmorillonite $Bi(NO_3)_3$, carbonyl compounds

1. Introduction

In multistep organic synthesis, there is a great importance of protection of functional groups [1]. There is a great interest now a days in protecting carbonyl compounds as cyclic and acyclic dithioacetals. The thioacetals show resistance towards hydrolytic cleavage under acidic and basic conditions[2]. 1,3-dithianes, in particular, are extensively used in the total synthesis of complex natural products[3]. Acylic dithioacetals particularly diethyldithioacetals are used for preparing open chain aldoses in the carbohydrate chemistry[4]. They oftenly serve as marked acyl anions in carbon-carbon bond forming reaction[5-6].

These compounds are generally synthesized by condensing carbonyl compounds with thiols or dithiols in presence of different reagents such as HCl[7] ,$BF_3.OEt_2$[8] or ZnCl2[9] as catalysts. Many other methods have been developed by using Lewis acids such as $AlCl_3$[10], $SiCl_4$[11], $InCl_3$[12], $NiCl_2$[13], Glycerol[14], HBA[15] NBS[16]. These methodologies have certain shortcomings such as tedious work up[10], inert atmospheric conditions[12] and expensive reagents[17].

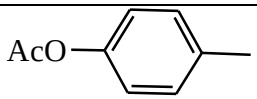
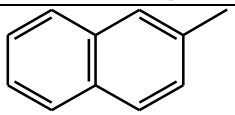
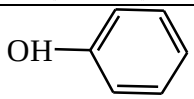
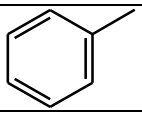
Herein, bismuth nitrate impregnated on montmorillonite K-10 is used as an efficient catalyst for the dithioacetalization of both aromatic and aliphatic carbonyl compounds by grinding at room temperature



Scheme - 1

Table 1: Thioacetalization of carbonyl compounds in presence of Montmorillonite-$Bi(NO_3)_3$

Product	R^1	R^2	Time(mts.)	Yield	m.p.(°C)
3a	$-C_6H_5$	H	10	97	73
3b	4-(OMe)C_6H_4	H	05	95	120
3c	2,4-(OMe)C_6H_3	H	04	98	103

3d		H	13	89	108
3e		H	9	93	112
3f		H	11	94	158
3g	C_6H_5-CH=CH-	H	09	85	62
3h	CH_3-$(CH_2)_4$-	H	12	30	--
3i	P-Cl-C_6H_4	H	20	90	--
3j		CH_3	15	95	Liq.

II. Results and Discussion

In this methodology, the protocol for the thioacetalisation consisted of aliphatic and aromatic carbonyl compounds, propane-1,3-dithiol and Montmorillonite – $Bi(NO_3)_3$, under solvent free conditions. The procedure involved the reaction between carbonyl compounds 1a-j and propane-1,3-dithiol 2 using Montmorillonite-$Bi(NO_3)_3$ catalyst by grinding in a pestle mortar at 25-28^oC. After completion of the reaction, the products 3a-j were extracted with diethyl ether. The solvent after evaporation furnished almost pure products.

Further, 4-hydroxybenzaldehyde and acetophenone in equimolar ratio on treatment with propane-1,3-dithiol with catalytic amount of Montmorillonite K-10-$Bi(NO_3)_3$ afforded only 1,3-dithiane derivative of 4-hydroxybenzaldehyde in 90% yield.

In summary a very simple and efficient synthetic protocol for thioacetalization of different carbonyl compounds in the presence of Montmorillonite-$Bi(NO_3)_3$ is reported. The advantages of this catalyst include low cost, commercial availability, chemoselectivity, solvent free conditions making it environment friendly and useful for industrial applications.

III. Experimental Section

Melting points are uncorrected and were determined on Perfit m.p. apparatus. Different reagents were purchased from Merck, Fluka, Aldrich. IR spectra were recorded on Perkin Elmer FTIR-1600 spectrophotometer as KBr disc. ^{1}H-NMR, ^{13}C-NMR spectra were recorded on a Bruker Advance DRX-400 spectrophotometer.

IV.General Procedure

Aldehyde (1 mol), propane-1,3-dithiol (1 mol) and Montmorillonite-$Bi(NO_3)_3$ were grinded in a pertle mortar at room temperature and continued until the reaction was complete. The reaction was monitored by TLC (Ethylacetate: n-hexane 3:7). After completion, the reaction mixture was extracted with diethylether and recrystallised from chloroform-petroleum ether.

V. Spectral data of the products

3a. 2-[Phenyl]-1,3-dithiane:

IR(KBr)cm^{-1}: 3037, 2940, 2894, 2827, 1593, 1491, 1429, 1281, 1183, 1066, 912, 728, 697.

^{1}H NMR(400 MHz, $CDCl_3$)δ: 1.87-1.98(m, 1H, H-5′), 2.10-2.19 (m, 1H, H-5″), 2.87-2.93(m, 2H, H-4), 3.00-3.07(m, 2H, H-6), 5.18(s, 1H, ArH-), 7.26-7.35(m, 3H, ArH), 7.47-7.49(m, 2H, ArH).

^{13}C-NMR(100MHz, $CDCl_3$)δ_C: 24.96, 31.95, 51.34, 127.61, 128.29, 128.59, 138.99.

3b. [4-Methoxyphenyl]-1,3-dithiane:

IR(KBr)cm^{-1}: 2929, 2909, 1613, 1511, 1439, 1253, 1178, 1111, 1040.

^{1}H NMR(400 MHz, $CDCl_3$)δ: 1.84-1.99(m, 1H, H-5′), 2.13-2.19(m, 1H, H-5″), 2.86-2.94(m,2H,H-4), 3.01-3.09(m, 2H, H-6), 3.78(s, 3H,-OCH_3), 5.13(s, 1H, ArH-), 6.86(d, 2H, J=8.61Hz, Ar-H), 7.39(d, 2H, J=8.58Hz, ArH).

^{13}C-NMR(100MHz, $CDCl_3$)δ_C: 24.05, 31.6, 49.71, 54.28, 113.05, 127.90, 130.29, 158.53.

Anal. Calcd. For $C_{11}H_{14}OS_2$: C: 58.38, H: 6.24, S: 28.35.

Found: C: 58.57, H: 6.21, S: 28.24.

3c. 2-[2,4-Dimethoxyphenyl]-1,3-dithiane:

IR(KBr)cm^{-1}: 2996, 2939, 2893, 2837, 1618, 1505, 1454, 1424, 1326, 1290, 1116, 1039, 992.

^{1}H NMR(400 MHz, $CDCl_3$): δ1.87 – 1.94(m, 1H, H-5′), 2.14-2.19(m, 1H, H-5″), 2.86-2.92(m, 2H, H-4), 3.07-3.16(m, 2H, H-6), 3.78(s, 3H, -OCH_3), 3.84(s, 3H, -OCH_3), 5.63(s, 1H, ArCH-1), 6.43(d, 1H, J=2.4Hz, ArH), 6.48(dd, 1H, J=2.4Hz, J = 8.5Hz, Ar-H), 7.48(d, 1H, J=8.5Hz, Ar-H).

^{13}C NMR(100MHz, $CDCl_3$)δ_C: 25.20, 32.41, 43.10, 55.30, 55.60, 98.50, 104.70, 119.80, 129.70, 156.40, 160.60.

Anal. Calcd. For $C_{12}H_{16}O_2S_2$.: C: 56.23, H: 6.28, S: 25.02.

Found: C: 56.02, H: 6.35, S: 25.13.

3d. 2(4-Acetoxyphenyl)-1,3-dithiane

IR(KBr)cm^{-1}: 2950, 2904, 2827, 1756, 1603, 1511, 1424, 1312, 1339, 1019, 922, 768.

^{1}H NMR(400 MHz, $CDCl_3$): δ1.88 – 1.99(m, 1H, H-5′), 2.14-2.18(m, 1H, H-5″), 2.27(s, 3H, -$OCOCH_3$), 2.87-2.93(m, 2H, H-4), 3.01-3.09(m, 2H, H-6), 5.18(s, 1H, ArH), 7.07(d, 2H, J=8.52Hz, ArH), 7.49(d, 2H, J = 2.4Hz, ArH), 6.49(dd, 1H, J = 2.4Hz, J = 8.5Hz, Ar-H), 7.48(d, 1H, J = 8.52Hz, Ar-H).

^{13}CNMR(100MHz, $CDCl_3$)δc: 21.07, 24.97, 31.96, 50.61, 121.74, 128.89, 136.61, 150.46, 169.19.

Anal. Calcd. For $C_{12}H_{14}O_2S_2$: C: 56.63; H: 5.53; S: 25.21.

Found: C: 56.51; H: 5.36; S: 25.25.

3e. 2-[Naphthyl]-1,3-dithiane

IR(KBr)cm^{-1}: 2939, 2899, 2827, 1608, 1511, 1429, 1280, 1178, 901, 829, 778.

^{1}H NMR(400 MHz, $CDCl_3$): δ1.94 – 2.05(m, 1H, H-5′), 2.14-2.26(m, 1H, H-5″), 2.88-2.98(m, 2H,H-4), 3.06-3.14(m, 2H, H-6), 5.33(s, 1H, ArCH-), 7.49(m, 2H, ArH), 7.59(dd, 1H, J = 1.5Hz, J = 8.7Hz, Ar-H), 7.78-7.84(m, 3H, Ar-H), 7.97(bs, 1H, ArH).

^{13}CNMR(100MHz, $CDCl_3$)δc: 25.1, 32.1, 51.5, 125.6, 126.3, 126.8, 127.6, 128.0, 128.4, 133.2, 133.3, 136.4.

3f. 2-[4-Hydroxyphenyl]-1,3-dithiane

IR(KBr)cm^{-1}: 3370, 2940, 2894, 2807, 1609, 1516, 1450, 1363, 1250, 1173, 1112, 851, 773.

^{1}H NMR(400 MHz, $CDCl_3$): δ1.88 – 1.99(m, 1H, H-5′), 2.15-2.20(m, 1H, H-5″), 2.87-2.93(m, 2H, H-4), 3.02-3.09(m, 2H, H-6), 5.14(s, 1H, ArCH-), 6.78(d, 2H, J = 8.2Hz, ArH), 7.33(d, 2H, J = 8.3Hz, ArH).

^{13}C NMR(100MHz, $CDCl_3$)δc: 25.01, 32.18, 50.74, 115.58, 129.18, 131.45, 155.6

Anal. Calcd. For $C_{12}H_{14}O_2S_2$: C: 56.58; H: 5.72; S: 30.22.

Found: C, 56.35; H, 5.64; S, 32.02.

3g. 2-Styryl-1,3-dithiane

IR(KBr)cm^{-1}: 3027, 2919, 2853, 1614, 1542, 1486, 1424, 1271, 1173, 1040, 963, 764, 697.

^{1}H NMR(400 MHz, $CDCl_3$): δ1.88 – 1.99(m, 1H, H-5′), 2.10-2.18(m, 1H, H-5″), 2.86-3.14(m, 4H, 2 x -SCH_2-), 4.83(d, 1H, J = 7.6Hz, ArCH), 6.28(dd, 1H, J = 7.8Hz, J=15.9 Hz, PhCH_2C*H*CH-), 6.78(d, 1H, J=15.6Hz, Ph*CH*=CHCH-), 7.23-7.33(m, 3H, ArH), 7.38-7.49(m,2H,ArH).

^{13}CNMR(100MHz, $CDCl_3$): δ25.18, 30.21, 47.66, 26.01, 126.65,128.08, 128.57, 133.37, 136.06

Anal. Calcd. For $C_{12}H_{14}S_2$: C: 64.80; H: 6.32; S: 28.82.

Found: C: 64.64; H: 6.22; S: 20.57.

3i. 2-[4-Chlorophenyl]-1,3-dithiane

IR(KBr)cm^{-1}: 3048, 2904, 2822, 1598, 1498, 1281, 1178, 1091, 1009, 830, 769, 671.

^{1}H NMR(400 MHz, $CDCl_3$): δ1.88-1.99(m, 1H, H-5′), 2.14-2.19(m,1H, H-5″), 2.88-2.94(m, 2H, H-4), 3.02-3.09(m, 2H, H-6), 5.14(s, 1H, ArCH-), 7.33(d, 2H, J=7.5 Hz, ArH), 7.42(d, 2H, J=7.5Hz, Ar-H).

Anal. Calcd. For $C_{10}H_{11}ClS_2$: C: 52.06; H: 4.82; S: 27.78.

Found: C: 52.23; H: 4.74; S: 27.63.

3j. 2-Methyl-2-Phenyl-1,3-dithiane

IR(KBr)cm^{-1}: 3063, 2909, 2832, 1603, 1496, 1440, 1308, 1286, 1189, 1071, 764, 702.

^{1}H NMR(400 MHz, $CDCl_3$): δ1.80(s, 3H, -CH3), 1.91-1.99(m, 2H, H-5′,5″), 2.74-2.79(m, 4H, 2x –SCH_2-), 7.24-7.28(m, 1H, Ar-H), 7.34-7.39(m, 2H, ArH),7.92-7.95(m,2H, ArH).

^{13}C NMR(100MHz, $CDCl_3$): δ24.57, 27.98, 32.67, 53.88, 126.95, 127.67, 128.45, 143.69.

Anal. Calcd. For $C_{12}H_{14}S_2$: C: 62.79; H: 6.70; S: 30.45.

Found: C: 62.57; H: 6.64; S: 30.11.

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