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Bromodimethylsulfonium bromide: A useful reagent for acylation of alcohols, phenols, amines, thiols, thiophenols and 1,1-diacylation of aldehydes under solvent free conditions

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Dedicated to A.C. Ghosh, Former Director, RRL-Jorhat, Assam on the occasion of his 65th birthday.

Abstract

Various alcohols and phenols, amines, thiols and thiophenols can be transformed easily to the corresponding acetate derivatives, on treating with two equivalent amount of acetic anhydride in the presence of 5 mol% bromodimethylsulfonium bromide pre-catalyst at room temperature in good yields. In addition, various aldehydes can also be converted to the corresponding *gem*-diacetates in good yields by employing 10 mol% of the same pre-catalyst using four equivalent amount of acetic anhydride. Some of the important features are: good yields, mild reaction conditions, no-aqueous work-up and chromatographic separation for a large-scale reaction, compatible with the substrates having other protecting groups and applicable to the carbohydrates and nucleosides. Interestingly, neither alkyl bromide formation from the corresponding alcohol nor bromination of the substrates took place under the experimental conditions.

Keywords: Acylation; Acetic anhydride; Alcohols and phenols; Amines; Thiols; Aldehydes; Catalytic synthetic protocol

1. Introduction

The acylation of alcohols and phenols, amines and thiols is one of the most useful and versatile transformations in organic synthesis [1]. Among them, the conversion of hydroxyl or amino group into the corresponding acetate is essential due to its medicinal value, e.g. the preparation of paracetamol from 4-aminophenol as well as for confirmation of the presence of hydroxyl or amino group in a compound. In addition, the protection of hydroxyl functionality as acetate is preferred due to its ease of introduction, stable under mild acidic reaction conditions and also ease of removal by mild alkaline hydrolysis. The acetylation of alcohols and phenols or amines is usually performed with acid anhydrides or acetyl chloride in the presence of amine bases such as triethylamine or pyridine or pyridine along with 4-(dimethylamino)pyridine (DMAP), which acts as a co-catalyst, or 4-pyrrolidinopyridine (PPY) [2]. Sometimes tributylphosphine (Bu_3P) is also employed as a less basic catalyst for acylation reactions particularly for the base sensitive substrates [3]. In the literature, several methods have been developed for the preparation of acetate from the corresponding alcohol or phenol or thiol using various metal salts, such as $CoCl_2$ [4], $ZnCl_2$ [5], $RuCl_3$ [6], $TiCl_4$–$AgClO_4$ [7], $LiClO_4$ [8], $Mg(ClO_4)_2$ [9], $Zn(ClO_4)_2{\cdot}6H_2O$ [10] and some triflates such as $Sc(OTf)_3$ [11], Me_3SiOTf [12], $In(OTf)_3$ [13], $Cu(OTf)_2$ [14], $Ce(OTf)_3$ [15] and $Bi(OTf)_3$ [16] as catalysts or stoichiometric reagents. Recently, it was reported that I_2 is also a useful catalyst for acetylation of alcohols under solvent

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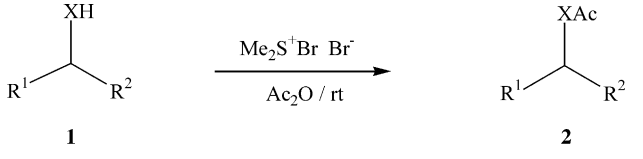


1 **2**

X = O / NH / S

R^1 = alkyl / aryl / sugar residue/ nucleoside residue;
R^2 = H, alkyl, aryl

Scheme 1.

free conditions [17]. Though perchlorates [8–10] have been found to be effective catalysts for this transformation, but there is a serious drawback such as some of the perchlorates are highly explosive [18]. In addition, $Mg(ClO_4)_2$ should be anhydrous in order to obtain better yields [9]. The other methods based on triflates [11–16] or $RuCl_3$ [6] have some disadvantages: (i) the reagents are expensive and some of them difficult to handle [12], (ii) long reaction times, (iii) dry reaction conditions [4] and (iv) invariably aqueous work-up and chromatographic separation procedure. Although numerous methods are known in the literature in order to obtain good yields of the acetylated products, still there is a great demand for mild and effective catalyst, which can be used for acetylation reaction to a wide variety of substrates. In continuation of our research programme to develop better and newer synthetic methodologies [19], we realized that bromodimethylsulfonium bromide, which can generate HBr in the reaction medium on reaction with alcohol [20], might be a very useful pre-catalyst for the acetylation reactions. The pre-catalyst, bromodimethylsulfonium bromide, has been utilized so far for the transformations of alcohols to the corresponding bromides [20], oxidation of thiols to the disulfides [21], deprotection of dithioacetals [22] and preparation of α-bromoenones from the corresponding enones [23]. Very recently, we have demonstrated tetrahydropyranylation/depyranylation of alcohols and phenols [24] as well as acetalization and thioacetalization of carbonyl compounds [25], and also oxathioacetalization of carbonyl compounds [26] using the same pre-catalyst. These successful results further encouraged us to study whether the same pre-catalyst could be implemented further for acylation reactions or not. In this paper, we wish to report the acetylation of alcohols and phenols, amines, thiols and thiophenols by employing acetic anhydride in the presence of a catalytic amount of bromodimethylsulfonium bromide as pre-catalyst under solvent free conditions, as shown in Scheme 1.

2. Result and discussion

For our present study, firstly bromodimethylsulfonium bromide was prepared according to the literature procedure [23]. Then, we attempted the acylation reaction of cetyl alcohol (**1a**) with acetic anhydride in the presence of 5 mol% of bromodimethylsulfonium bromide at room temperature. We have noticed that the reaction was completed within 20 min and the pure acetate derivative of cetyl alcohol (**2a**) was obtained in 96% yield as a gummy liquid. The product was characterized by recording IR, ^{1}H NMR spectra and elemental analysis and is agreeable with the acetate. Next, we examined that benzoyl, benzyl, tosyl and *tert*-butyldimethylsilyl ether protected alcohols **1b–e** were converted smoothly to the corresponding acetates **2b–e** in good yields without affecting the protecting groups by following identical reaction conditions. All the products were characterized by recording IR, ^{1}H NMR spectra and elemental analyses. Likewise, various benzylic alcohols (**1f–k**), secondary alcohol (**1l**), allyl alcohol (**1m**) and 1,4-butynediol (**1n**) were also provided the corresponding acetate derivatives **2f–n** in good yields. It is interesting to mention that neither alkyl bromide formation from the corresponding alcohols nor HBr addition took place at the double bond or even at the triple bond during the experimental conditions. It was observed that the alkyl TBS ether did not survive during acetylation by employing $Ce(OTf)_3$ [15] as catalyst. However, our protocol has some advantage because the TBS group was unaffected during the reaction conditions. Moreover, a tertiary alcohol (**1o**) as well as a sterically hindered tertiary alcohol adamantanol (**1p**) was smoothly converted to the corresponding acetate derivatives **2o** and **2p**, respectively, without the formation of elimination product. The product **2o** was also confirmed by recording ^{13}C NMR spectrum as well as ^{1}H NMR spectrum. We have noticed that the present method is more efficient in terms of reaction timing as compared to the ruthenium(III) chloride method [6] particularly for the preparation of **2p**. After that we wanted to investigate the versatility of the reagent for acetylation of phenolic compounds. By using our protocol, the phenolic compounds **1q** and **1r** were transformed smoothly to the corresponding acetate derivatives **2q** and **2r**. Again, we have observed that 4-nitrophenol (entry **1r**) was converted to the acetate derivatives much faster as compared to the earlier reported procedure [6]. Remarkably, an alcohol containing isopropylidene group **1s** can also be acetylated under identical conditions without cleavage of the isopropylidene group. Next, we intended to further study whether the present methodology could be extended for acetylation of carbohydrates and nucleosides. We have found that various carbohydrate molecules, such as **1t–v** and thymidine (**1w**) were converted to the corresponding acetate derivatives **2t–w** in good yields under identical reaction conditions. Importantly, thio- and methoxyl group at the anomeric position were unaffected during experimental conditions. The reaction times and yields of the products are summarized in the Table 1. All the acetylated products were characterized by recording IR, ^{1}H NMR spectra and elemental analyses, and in full agreement with the expected products. By using our protocol, aliphatic and aromatic amines (entry **1x–y**) as well as thiols (entry **1z** and **1a′**) were transformed to the corresponding acetate derivatives **2x–a′** in good yields by employing the same pre-catalyst.

Table 1
Preparation of various acetate derivatives **2** from the corresponding hydroxyl compounds, amines and thiols **1** using bromodimethylsulfonium bromide as pre-catalyst

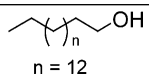
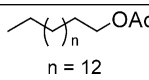
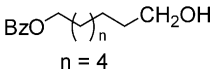
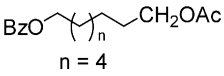
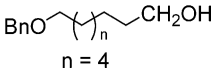
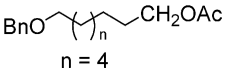
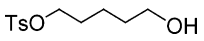
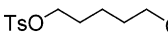
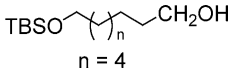
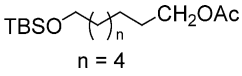
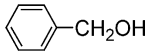
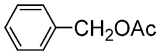
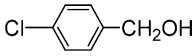
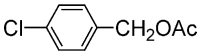
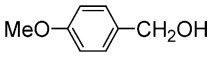
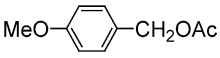
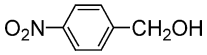
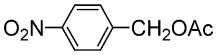
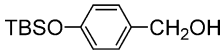
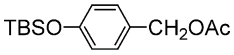
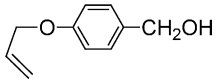
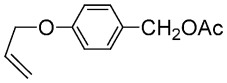
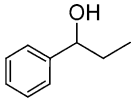
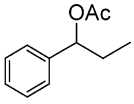
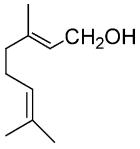
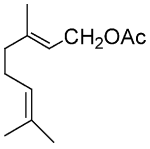
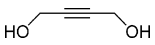
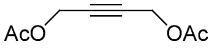
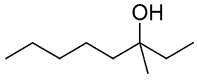
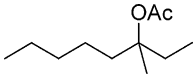
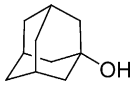
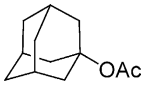
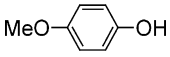
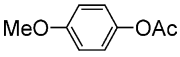
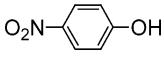
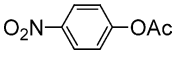
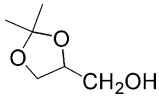
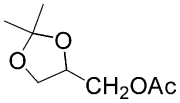
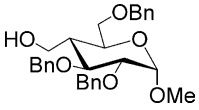
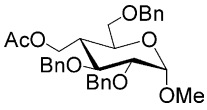
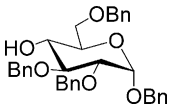
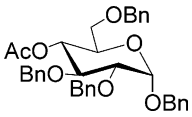
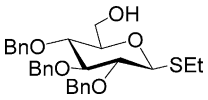
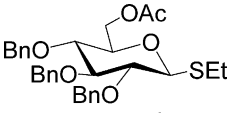
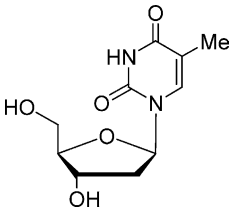
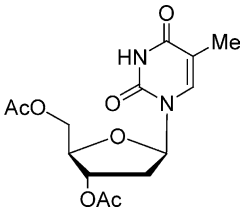
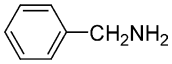
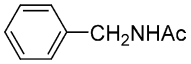
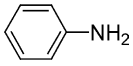
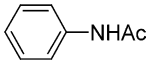
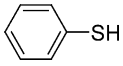
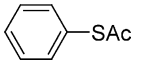
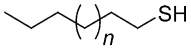
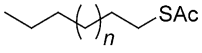
Entry	Substrate (**1**)	Time (min)	Product[a] (**2**)	Yield[b] (%)
a		20		90
b		25		92
c		30		88
d		25		86
e		25		85 [47]
f		25		90 [48]
g		35		92 [28]
h		30		90 [27]
I		30		87 [28]
j		20		85
k		30		82
l		35		95
m		30		90 [48]
n		70		82
o		60		70
p		40		91 [29]
q		30		90 [30]
r		90		87 [30]
s		30		80 [10]
t		60		85

Table 1 (*Continued*)

Entry	Substrate (**1**)	Time (min)	Product[a] (**2**)	Yield[b] (%)
u		120		80
v		60		83
w		180		85 [48]
x		20		87
y		30		88 [48]
z		50		92 [48]
a′	 *n* = 7	35	 *n* = 7	83

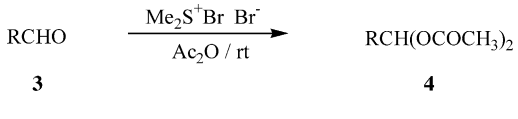
[Ref.]: The spectroscopic data is reported for the acetate derivative.

[a] Products **2** were characterized by IR, ^{1}H NMR spectra and elemental analysis.

[b] Isolated yield.

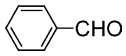
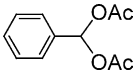
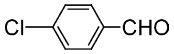
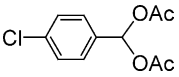
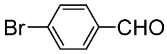
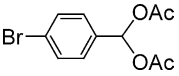
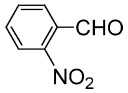
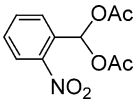
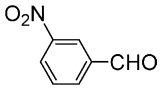
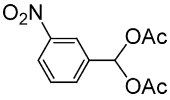
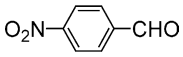
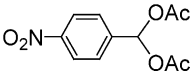
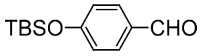
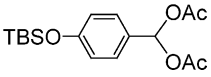
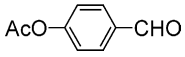
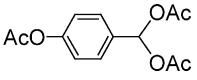
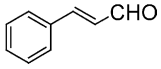
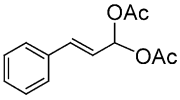
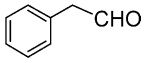
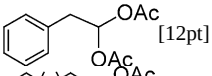
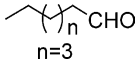
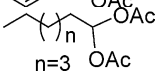
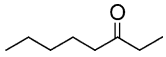
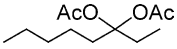
Notably, we have noticed that the conversion of the hydroxyl compounds to the respective acetate derivatives can be carried out even in a larger scale (100 mmol) without any difficulty by using 2 mmol of the pre-catalyst instead of required 5 mmol of pre-catalyst. For instance, when a mixture of benzyl alcohol (100 mmol) and acetic anhydride (175 mmol) was treated with 2 mmol of bromodimethylsulfonium bromide, it was smoothly converted to the acetate **2f** in 95% yield within 30 min. From this result, it indicates that a large-scale reaction is possible using a less amount of bromodimethylsulfonium bromide pre-catalyst. It is important to point out that the present method is much more cleaner, does not involve any aqueous work-up and chromatographic separation for a large-scale reaction.

Lastly, our aim was to explore the possibility for 1,1-diacetylation of aldehydes by involving the same reagent. The formation of geminal diesters from the corresponding aldehydic compound is an important organic transformation because they serve as building blocks for asymmetric allylic alkylation [31] and Diel's Alder reaction [32]. Moreover, acylals are more oftently used as protecting groups for aldehydes because they are stable under neutral and basic conditions [33]. The formation of 1,1-diacetate is usually achieved by the reaction of aldehydic compound with acetic anhydride in the presence of an acid or Lewis acid, which act as a catalyst. Some of the reagents and catalysts that have recently been employed for similar transformation, such as LiOTf [34], ceric ammonium nitrate [35], $InCl_3$ [36], H_2NSO_3H [37], $LiBF_4$ [38], H_2SO_4 [39], PCl_3 [40], NBS [41], I_2 [42], TMSCl-NaI [43], $FeCl_3$ [44] and $Bi(NO_3)_3{\cdot}5H_2O$ [45]. Some metal triflates, such as $Cu(OTf)_2$ [46a] and $Sc(OTf)_3$ [46b] have also been utilized as catalysts for the preparation of 1,1-diacetate derivatives from the corresponding aldehydes. Many of these methods have certain drawbacks, such as long reaction time, involvement of expensive reagents and sometimes it is failure to prepare acylals for aliphatic aldehyde or for an electron-rich aromatic aldehyde [35]. Therefore, there is a scope to find out an alternative method, which might be mild and catalytically efficient. By using the same pre-catalyst, various aldehydes were converted smoothly to the corresponding 1,1-diacetates as shown in Scheme 2.



Scheme 2.

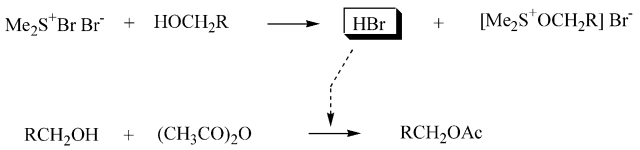
Table 2
Preparation of various 1,1-diacetate **4** from the corresponding aldehydes **3** using bromodimethylsulfonium bromide as pre-catalyst

Run	Substrate (**3**)	Time (h)	Product[a] (**4**)	Yield[b] (%)
a		3.0		85 [40]
b		3.5		84 [41]
c		3.0		89
d		4.5		87 [45a]
e		4.0		85 [45b]
f		4.5		89 [41]
g		4.0		80 [34]
h		5.0		82 [49]
I		5.5		74 [43]
j		[1]	 [12pt]	82
k		5.0		73
m		[2]		0

[Ref]: The spectroscopic data is available for the gem-diacetate.
[a] Products **4** were characterized by IR, ^{1}H NMR spectra and elemental analysis.
[b] Isolated yield.

When benzaldehyde (5 mmol) was treated with acetic anhydride (20 mmol) in presence of 0.5 mmol of bromodimethylsulfonium bromide at room temperature, it was smoothly converted to the corresponding *gem*-diacetate derivative within 3 h in good yield. Likewise, various aromatic aldehydes **3b**–**h** were converted into the corresponding 1,1-diacetates **4b**–**h**, respectively, in good yields. Similarly, the α,β-unsaturated aldehyde **3i** gave the corresponding diacetate **4i** keeping the double bond intact The reaction times and yields of the 1,1-diacetates are mentioned in Table 2. All the products were characterized by recording melting point, IR, ^{1}H NMR spectra and elemental analysis. In addition, the melting point was verified with the reported melting point. Moreover, the aliphatic aldehydes **3j** and **3k** were transformed into the *gem*-diacetates **4j** and **4k** in a similar manner. It is important to mention that neither α-bromination nor cyclotrimerization was observed during the experimental conditions. Nevertheless, both aliphatic and aromatic aldehydes can be converted to the corresponding diacetates in good yields. By following the same procedure, acetophenone did not provide any *gem*-diacetates, on treating with acetic anhydride in the presence of the same pre-catalyst.

The formation of the products can be rationalized as follows. It has been proposed that bromodimethylsulfonium bromide may generate HBr in the medium on reaction with methanol [20]. We believe that in situ generated HBr catalyzes the acetylation reaction of alcohols and phenols, amines, thiol and thiophenols and aldehydes into the cor-



Scheme 3.

responding acetates derivatives (Scheme 3). It is also noted that the pH of the solution is ~2–3 during the reaction.

3. Experimental

IR spectra are recorded in KBr or neat on a Nicolet Impact 410 spectrophotometer. ^{1}H NMR spectra are recorded on Jeol 400 MHz and Brucker 300 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.

3.1. General procedure for acetylation

To a mixture of alcohols/phenols/amines/thiols/thiophenols (10 mmol) and acetic anhydride (2.1 mL, 20.0 mmol) was added the pre-catalyst bromodimethylsulfonium bromide (111 mg, 0.5 mmol) at room temperature and left for stirring at the same temperature. After completion of the reaction as indicated by TLC, the reaction mixture was co-evaporated three times by adding 20 mL of toluene to remove acetic acid and other by-products. The crude product was found to be reasonably pure. The spectroscopic grade compound can be obtained by distillation under reduced pressure in case of a liquid or by recrystallization in case of a solid. Similarly, aldehydes were converted to the 1,1-diacetates by using acetic anhydride (40 mmol) and 1 mmol of pre-catalyst. The products were isolated as stated above.

Compound 2a. Colourless liquid; IR (Neat): 2919, 2858, 1747 (CO), 1465, 1368, 1235, 1045 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 7.2 Hz, –CH_3), 1.22–1.36 (m, 26H, –CH_2), 1.48–1.62 (m, 2H, –CH_2), 2.04 (s, 3H, –$COCH_3$), 4.04 (t, 2H, J = 7.2 Hz, –OCH_2) ppm. Anal. Calcd. for $C_{18}H_{36}O_2$ (284.48): C, 76.00; H, 12.75%. Found: C, 75.82; H, 12.69%.

Compound 2b. Colourless liquid; IR (Neat): 3063, 2930, 2858, 1731 (CO), 1593, 1455, 1378, 1271, 1240, 1112, 1035 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30–1.50 (m, 8H, –CH_2), 1.60–1.70 (m, 2H, –CH_2), 1.72–1.80 (q, 2H, –CH_2), 2.04 (s, 3H, –$COCH_3$), 4.05 (t, 2H, J = 7.2 Hz, –OCH_2), 4.32 (t, 2H, J = 6.8 Hz, –OCH_2), 7.44 (t, 2H, J = 8.0 Hz, ArH), 7.55 (t, 1H, J = 8.0 Hz, ArH), 8.04 (d, 2H, J = 7.6 Hz, ArH) ppm. Anal. Calcd. for $C_{17}H_{24}O_4$ (292.37): C, 69.84; H, 8.27%. Found: C, 69.70; H, 8.21%.

Compound 2c. Colourless liquid; IR (Neat): 2931, 2856, 1740 (CO), 1454, 1365, 1240, 1099, 1033 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21–1.32 (m, 8H, –CH_2), 1.50–1.56 (m, 4H, –CH_2), 1.97 (s, 3H, –$COCH_3$), 3.39 (t, 2H, J = 6.6 Hz, –OCH_2), 3.97 (t, 2H, J = 6.8 Hz, –OCH_2), 4.43 (s, 2H, –CH_2Ph), 7.19–7.29 (m, 5H, ArH) ppm. Anal. Calcd. for $C_{17}H_{26}O_3$ (278.39): C, 73.35; H, 9.41%. Found: C, 73.08; H, 9.32%.

Compound 2d. Colourless liquid; IR (Neat): 2945, 1863, 1737 (CO), 1373, 1598, 1460, 1368, 1250, 1183, 1040 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11–1.66 (m, 6H, –CH_2), 1.96 (s, 3H, –$COCH_3$), 2.38 (s, 3H, –CH_3), 3.94 (t, 2H, J = 6.5 Hz, –OCH_2), 3.96 (t, 2H, J = 6.4 Hz, –OCH_2), 7.35 (d, 2H, J = 8.3 Hz, ArH), 7.79 (d, 2H, J = 8.3 Hz, ArH) ppm. Anal. Calcd. for $C_{14}H_{20}O_5S$ (300.37): C, 55.98; H, 6.71, S, 10.68%. Found: C, 55.73; H, 6.79, S, 10.45%.

Compound 2j. Colourless liquid; IR (Neat): 2954, 2930, 2888, 2859, 1747 (CO), 1610, 1521, 1237, 1229, 913 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 6H, $Si(CH_3)_2$), 0.98 (s, 9H, –$SiC(CH_3)_3$), 2.08 (s, 3H, –$COCH_3$), 5.02 (s, 2H, –OCH_2), 6.81 (d, 2H, J = 8.0 Hz, ArH), 7.22 (d, 2H, J = 8.0 Hz, ArH) ppm. Anal. Calcd. for $C_{15}H_{24}SiO_3$ (280.44): C, 64.24; H, 8.63%. Found: C, 64.59; H, 8.55%.

Compound 2k. Viscous liquid; IR (Neat): 3083, 2965, 2868, 1746 (CO), 1623, 1516, 1460, 1388, 1367, 1239, 1183, 1040 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 3H, –$COCH_3$), 4.53 (d, 2H, J = 5.1 Hz, –OCH_2), 5.03 (s, 2H, –CH_2Ph), 5.28 (dd, 1H, J = 1.5 Hz, J = 10.8 Hz, =CH_2), 5.40 (dd, 1H, J = 1.5 Hz, J = 17.4 Hz, =CH_2), 5.98–6.11 (m, 1H, =CH), 6.90 (d, 2H, J = 8.7 Hz, ArH), 7.28 (d, 2H, J = 8.7 Hz, ArH) ppm. Anal. Calcd. for $C_{12}H_{14}O_3$ (206.24): C, 69.89; H, 6.84%. Found: C, 69.75; H, 6.75%.

Compound 2l. Colourless liquid; IR (Neat): 3063, 3022, 2976, 2925, 2879, 1742 (CO), 1491, 1460, 1378, 1250, 1055 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, J = 7.2 Hz, –CH_3), 1.81–195 (m, 2H, –CH_2), 2.07 (s, 3H, –$COCH_3$), 5.66 (t, 1H, J = 7.2 Hz, –CHOAc), 7.20–7.37 (m, 5H, ArH) ppm. Anal. Calcd. for $C_{11}H_{14}O_2$ (178.23): C, 74.13; H, 7.92%. Found: C, 74.01; H, 7.85%.

Compound 2n. Colourless low melting solid; IR (Neat): ν 2949, 1752 (CO), 1435, 1383, 1222, 1156, 1038 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 6H, 2× –$COCH_3$), 4.71 (s, 4H, 2× –OCH_2) ppm. Anal. Calcd. for $C_8H_{10}O_4$ (170.16): C, 56.47; H, 5.92%. Found: C, 56.19; H, 5.85%.

Compound 2o. Colourless liquid; IR (Neat): 2935, 2873, 1737 (CO), 1465, 1373, 1250, 1143, 1025 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, 3H, J = 8.0 Hz, –CH_3), 0.89 (t, 3H, J = 7.2 Hz, –CH_3), 1.24–1.34 (m, 6H, –CH_2), 1.37 (s, 3H, –CH_3), 1.62–1.90 (m, 4H, –CH_2), 1.97 (s, 3H, –$COCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.13, 14.17, 22.48, 22.72, 23.37 (2C), 30.91, 32.25, 37.81, 85.13, 170.18 ppm. Anal. Calcd. for $C_{11}H_{22}O_2$ (186.29): C, 70.92; H, 11.90%. Found: C, 70.76; H, 11.85%.

Compound 2p. Low melting solid; IR (Neat): 2940, 2852, 1746 (CO), 1365, 1243, 1095, 1042 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60–1.70 (bs, 6H, –CH_2), 1.96 (s, 3H, –$COCH_3$), 2.10 (bs, 6H, –CH_2), 2.15 (bs, 3H, –CH) ppm. Anal. Calcd. for $C_{12}H_{18}O_2$ (194.27): C, 74.19; H, 9.34%. Found: C, 74.01; H, 9.28%.

Compound 2t. Colourless liquid; IR (Neat): 3032, 2899, 1742 (CO), 1455, 1363, 1240, 1091, 1055 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (s, 3H, –$COCH_3$), 2.07 (m, 1H, H-4), 3.39 (s, 3H, –OCH_3), 3.59–3.63 (m, 3H), 3.82–3.88 (m, 1H, H-5), 3.90 (t, 1H, J = 9.2Hz, H-3), 4.01 (dd, 1H, J = 2.4 Hz, J = 11.4 Hz, H-6), 4.32 (dd, 1H, J = 2.8 Hz, H-6′), 4.47 (d, 1H, J = 12.0 Hz, –OCHPh), 4.58 (d, 1H, J = 10.8 Hz, –OCHPh), 4.60 (d, 1H, J = 12.0 Hz, –OCHPh), 4.66 (d, 1H,

J = 12.0 Hz, –OCHPh), 4.69 (d, 1H, J = 3.6 Hz, H-1), 4.78 (d, 1H, J = 12.0 Hz, –OCHPh), 4.96 (d, 1H, J = 10.8 Hz, –OCHPh), 7.22–7.40 (m, 15H, ArH) ppm. Anal. Calcd. for $C_{31}H_{36}O_7$ (520.62): C, 71.52; H, 6.97%. Found: C, 71.25; H, 6.90%.

Compound 2u. Colourless liquid; IR (Neat): 3065, 3030, 2918, 2867, 1748 (CO), 1503, 1457, 1376, 1234, 1101, 1045 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.83 (s, 3H, $–COCH_3$), 3.40–3.44 (m, 2H), 3.59 (dd, 1H), 3.83–3.87 (m, 1H), 3.97 (t, 1H), 4.46–4.56 (m, 4H), 4.62–4.71 (m, 3H), 4.82 (d, 1H, J = 3.6 Hz, H-1), 4.90 (d, 1H, J = 12.0 Hz), 5.04 (t, 1H, J = 8.0 Hz), 7.25–7.40 (m, 20H, ArH) ppm. Anal. Calcd for $C_{36}H_{38}O_7$ (582.69): C, 74.20; H 6.57%. Found: C, 74.01; H, 6.60%.

Compound 2v. Solid, mp 63 °C; IR (KBr): 3063, 3027, 2925, 2868, 1737 (CO), 1455, 1363, 1235, 1071 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (t, 3H, J = 7.6 Hz, $–SCH_2\mathit{CH_3}$), 2.03 (s, 3H, $–COCH_3$), 2.64–2.80 (m, 2H, $–S\mathit{CH_2}CH_3$), 3.44 (t, 1H, J = 9.2 Hz), 3.50–3.52 (m, 1H, H-5), 3.54 (t, 1H, J = 9.6 Hz), 3.71 (t, 1H, J = 8.8 Hz), 4.19 (dd, 1H, J = 4.4 Hz, J = 11.6 Hz, H-6), 4.33 (dd, 1H, J = 1.6 Hz, J = 12.0 Hz, H-6′), 4.47 (d, 1H, J = 9.6 Hz, H-1), 4.57 (d, 1H, J = 11.2 Hz, –OCHPh), 4.74 (d, 1H, J = 10.4 Hz, –OCHPh), 4.85 (d, 1H, J = 10.8 Hz, –OCHPh), 4.86 (d, 1H, J = 10.8 Hz, –OCHPh) 4.92 (d, 1H, J = 10.4 Hz, –OCHPh), 4.95 (d, 1H, J = 10.8 Hz, –OCHPh), 7.26–7.36 (m, 15H, ArH) ppm. Anal. Calcd. for $C_{31}H_{36}O_6S$ (536.68): C, 69.38; H, 6.76; S, 5.97%. Found: C, 69.23; H, 6.70, S, 5.70%.

Compound 2x. mp 61–62 °C; IR (Neat): 3298, 3068, 3027, 2925, 2884, 1650 (CO), 1557, 1455, 1383, 1281, 1081, 1009 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H, $–COCH_3$), 4.41 (d, 2H, J = 5.2 Hz, $–NCH_2Ar$), 5.92 (bs, 1H, –NH), 7.22–7.40 (m, 5H, ArH) ppm. Anal. Calcd. for $C_9H_{11}NO$ (149.19): C, 72.46; H, 7.43; N, 9.39%. Found: C, 72.19; H, 7.36; N, 9.30%.

Compound 2a′. Colourless liquid; IR (Neat): 2940, 2853, 1692 (CO), 1460, 1342, 1132, 948 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 7.2 Hz, $–CH_3$), 1.20–1.40 (m, 18H, $–CH_2$), 1.45–1.60 (m, 2H, $–CH_2$), 2.32 (s, 3H, $–COCH_3$), 2.86 (t, 2H, J = 7.6 Hz, $–SCH_2$) ppm. Anal. Calcd. for $C_{14}H_{28}SO$ (244.44): C, 68.79; H, 11.55; S, 13.12%. Found: C, 68.49; H, 11.49; S, 12.97%.

Compound 4c. Solid, mp 84 °C; IR (KBr): 3063, 2986, 2930, 1762 (CO), 1593, 1486, 1378, 1245, 1214, 1076, 1015, 968 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 6H, 2× $COCH_3$), 7.39 (d, 2H, J = 8.4 Hz, ArH), 7.53 (d, 2H, J = 8.8 Hz, ArH), 7.61 (s, 1H, $C\mathit{H}(OAc)_2$) ppm. Anal. Calcd. for $C_{11}H_{11}BrO_4$ (287.10): C, 46.02; H, 3.86%. Found: C, 46.21; H, 3.80%.

Compound 4j. Colourless liquid; IR (Neat): 3063, 3032, 2930, 1757 (CO), 1603, 1496, 1424, 1273, 1209, 1086, 1009 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.94 (s, 6H, 2× $COCH_3$), 2.97 (d, 2H, J = 5.7 Hz, $–CH_2Ph$), 6.84 (t, 1H, J = 5.7 Hz, $C\mathit{H}(OAc)_2$), 7.07–7.26 (m, 5H, ArH) ppm. Anal. Calcd. for $C_{12}H_{14}O_4$ (222.24): C, 64.85; H, 6.35%. Found: C, 64.78; H, 6.29%.

Compound 4k. Colourless liquid; IR (Neat): 2930, 2863, 1762 (CO), 1465, 1378, 1250, 1214, 1112, 1015, 968 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, 3H, J = 6.8 Hz, CH_3), 1.22–1.40 (m, 8H, $–CH_2$), 1.66–1.80 (m, 2H, $–CH_2$), 2.07 (s, 6H, 2× $COCH_3$), 6.77 (t, 1H, $C\mathit{H}(OAc)_2$) ppm. Anal. Calcd. for $C_{11}H_{20}O_4$ (216.28): C, 61.09; H, 9.32%. Found: C, 60.89; H, 9.27%.

4. Conclusion

We have developed a simple, efficient and catalytic method for the preparation of acetates from the corresponding alcohols and phenols, amine, thiols, thiophenols and aldehydes by employing bromodimethylsulfonium bromide as pre-catalyst under solvent free conditions without chromatographic separation. It is important to mention that alkyl bromide formation from the corresponding alcohols and bromination did not take place under the experimental conditions. Due to its operational simplicity, generality and efficacy, this method is expected to have wider applicability for the acylation reaction of alcohols and phenols, amine, thiols, thiophenols and aldehydes.

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