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DABCO: an efficient promoter for the acetylation of carbohydrates and other substances under solvent-free conditions

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ABSTRACT

A simple, mild and efficient solvent-free method for the acetylation of carbohydrates, and their partially protected derivatives, as well as non-carbohydrate substances in excellent yields in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) is described with the advantage of tolerance to various functional groups, short reaction time and ease of product isolation.

Per-O-acetylated hexopyranoses are widely used starting materials for the synthesis of biologically important oligosaccharides and glycoconjugates.[1] Besides, structural elucidation of many polyhydroxylic natural products is very often facilitated by transformation into their corresponding acetates. Due to the high solubility of sugar acetates in both liquid and supercritical CO_2 they are widely used as biocompatible and non-toxic renewable materials for the preparation of functional surfactants for micro emulsion systems; and they show promise as excipient systems for the pharmaceuticals and as novel co-solvents in biological applications to reduce the excessive waste of organic solvents utilized in processing.[2a,b] Separation and fixation of acidic green house gas (CO_2) currently being of great environmental concern, sugar acetates, like ionic liquids, hold great potential to be used as materials for the separation of CO_2 from sources such as natural gas and various prepared fuel gases.[2c] The procedure most often used for the acetylation of sugar alcohols involves the use of a large excess of acetic anhydride along with pyridine that serves as a catalyst cum solvent for the reaction.[3] Use of pyridine derivatives, for example, 4-(*N*,*N*-dimethylamino) pyridine, 4-(1-pyrrolidino)pyridine, etc as co-catalyst to speed up this transformation is also widely practiced.[4] However, pyridine and its derivatives are very toxic in nature, having unpleasant odor and are not easy to remove. Acetylation using imidazole, another basic catalyst, reported recently requires the use of acetonitrile, a toxic agent, as the solvent.[5] Methods that are environmentally more benign but involving acidic catalysts such as molecular I_2,[6] and $In(OTf)_3$[7] for the per-O-acetylation of sugars reported in the recent past employs a neat condition for the reaction but using excess acetic anhydride. Other catalysts that have been shown to be effective for this purpose include Bronstead acids, such as H_2SO_4,[8a] $HClO_4$,[8b] along with its supported system $HClO_4$-silica,[9] are also effective but their application gets limited due to the incompatibility with acid labile groups when present in the molecule. Heterogeneous catalysts such as Montmorillonite K-10[10] and others also serve as catalysts for the acetylation but isomerization (leading to mixtures of pyranose- and furanose forms) and longer reaction times have been of great concern. Lewis acid catalysts such as $ZnCl_2$,[11] metal triflates,[12a–h] trimethylsilyl triflate,[12i] etc are also versatile promoters of acetylation reaction. But the cost/availability/toxicity/ and difficulty in handling (mainly because of their sensitivity to moisture/air) can limit the application of these agents. Indium chloride-method reported on the other hand requires microwave irradiation in acetic anhydride.[12j] In contrast to the many reports on acetylation using acidic catalysts, only a very few reports are available in the literature on basic catalysts serving the purpose. Our laboratory has been engaged in the exploration of practical green chemistry that eliminates the use of substances hazardous to human health and environment[13] and recently we have reported solvent-free syntheses of thioglycosides[13a] and glycosyl azides[13b] as well as regioselective tritylation of hexosides and nucleotides.[13c,d] The latter methods employ 1,4-diazabicyclo[2.2.2]octane (DABCO) as the base catalyst and thus eliminate the need for using pyridine, a toxic solvent, most often employed as catalyst cum solvent for such reactions. On the other hand DABCO has been reported to be considerably less toxic than

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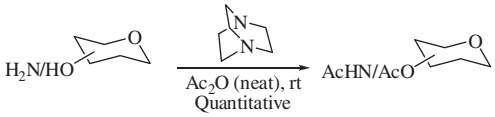


Scheme 1. DABCO-mediated acetylation of carbohydrates.

pyridine.[13e] Herein we like to report another practical application of DABCO as an efficient, inexpensive and easy to handle reagent for the acetylation of various carbohydrates using acetic anhydride as the acetylating agent (Scheme 1).

A set of initial experiments carried out using the commercially available methyl α-D-glucopyranoside (Table 1, entry 1) as the substrate revealed that a molar ratio of the sugar:Ac_2O:DABCO = 1:5

Table 1
DABCO-mediated acetylation of carbohydrates, their derivatives and non-carbohydrate substances[a]

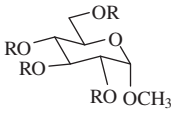
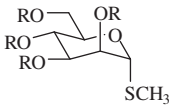
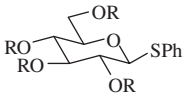
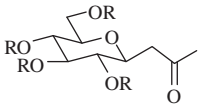
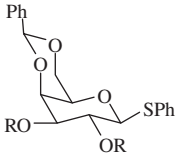
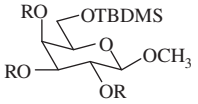
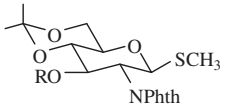
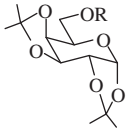
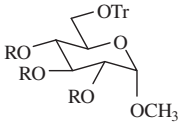
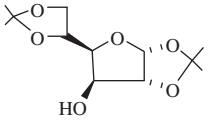
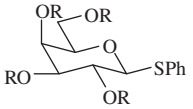
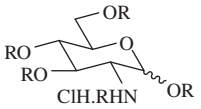
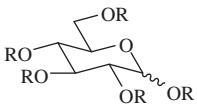
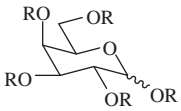
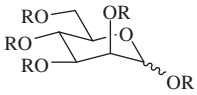
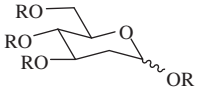
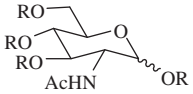
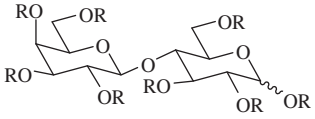
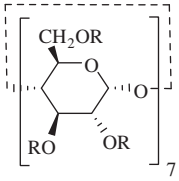
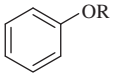
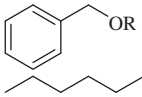
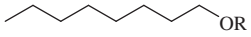
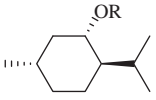
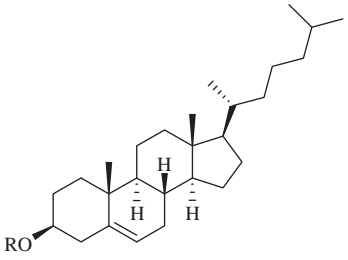
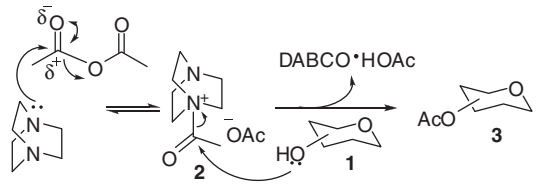
Entry	Compound structure: R = H → R = Ac	Reaction		Refs.
		Time (min)	Yield (%)	
1		55	97	16
2		35	95	17
3		25	95	12d
4		50	94	9
5		25	96	18
6		65	98	10e
7		15	96	18
8		25	98	19
9[b]		45	94	13d
10		30	96	20
11		80	97	5
12		240	96 (α - only)	21

Table 1 (*continued*)

Entry	Compound structure: R = H → R = Ac	Reaction		Refs.
		Time (min)	Yield (%)	
13[c]		60	95 (α:β = 1.53:1)	12d
14		230	94 (α:β = 5.35:1)	12d
15		130	95 (α:β = 1.85:1)	12d
16		55	95 (α:β = 0.27:1)	22
17		200	97 (α - only)	22
18		420	94(α:β = 0.46:1)	5
19[d]		270	96	23
20		30	97	12f
21		20	95	12f
22		30	95	12f
23		40	94	12f
24		65	94	12f

[a] Substrate (1 g) with Ac_2O, 1.2 mol equiv per OH/NH_2 group and DABCO, 1.0 mol equiv were used for the reaction under neat condition.
[b] Methyl α-D-glucopyranoside was converted to methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranoside in one-pot on 10 g scale. The time reported is for the two steps combined.
[c] The reaction carried out was on 10 g scale.
[d] The reaction was carried out at 55 °C.

(1.2 mol equiv per OH group):1 was optimal for the reaction. Under these conditions a facile reaction took place leading to the formation of the desired methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside[14] in a virtually quantitative yield. The authenticity of the product was obtained from its NMR spectroscopic data and a comparison of the physical constants with literature data. It may be emphasized that as the per-O-acetylated product is insoluble in water, it could be obtained as a colorless solid upon the addition of crushed ice to the reaction mixture and separation by filtration and drying. The product could be made free of the amine and its salt by washing with cold water, thus eliminating the need for an acidic work-up as usually is the case at the instance of pyridine in the classical method. The proposed mechanism for the acetylation of sugars is shown in Scheme 2 in which the role of DABCO is



Scheme 2. Proposed mechanism for the DABCO-mediated acetylation of carbohydrates.

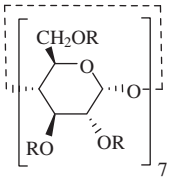
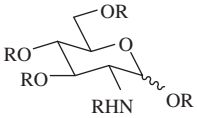
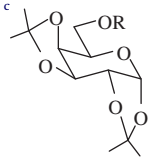
essentially as an acyl transfer agent. Thus, the initial reaction of one of the nucleophilic nitrogens in the molecule with Ac_2O can give rise to the N-acetylated intermediate **2** which upon reaction with the alcoholic functionality of sugar **1** would lead to the formation of the desired acetate **3** after the deprotonation assisted by the acetate base (Scheme 2).

In order to establish the effectiveness and the acceptability of the method in a wider context of synthetic carbohydrate chemistry, acetylation of a variety of carbohydrates and their derivatives was subsequently carried out and the results are presented in Table 1. In all the cases studied clean and complete conversion was observed and the respective per-O-acetylated product desired was isolated in essentially quantitative yield without the need for purification by column chromatography. The anomeric ratio (α:β) of the acetylated product obtained in the case of the reducing sugars was determined by ^1H NMR spectroscopic analysis of the isolated product mixture. Importantly, no furanosyl acetates were found to be formed in the case of free sugars (Table 1, entries 12–17) as evidenced by the NMR spectra of the acetylated products isolated. In general, the completely unprotected sugars underwent acetylation slower than their partially protected analogues (Table 1, entries 12–19) as to be expected from their relative solubility characteristics in acetic anhydride. Again, as was expected, the most common protecting groups such as TBDMS, TBDPS, trityl, benzylidene and isopropylidene groups were very stable under the conditions of acetylation. All reactions could be effectively carried out at room temperature except that of β-cyclodextrin (Table 1, entry 19) which required approximately 50 °C for the reaction to be completed in a reasonably short time period. A multi-gram scale (10 g) reaction (Table 1, entry 13) carried out was also proved very effective yielding the desired per-O-acetylated product, again, in nearly quantitative isolated yield. Moreover, the reactions carried out on multi-gram quantities were significantly faster compared to those using a gram (or less) of the starting material, the heat of reaction helping in the acceleration of the reaction rate in the former (see Table 1, entry 13). One-pot successive tritylation (regioselective) and acetylation could also be carried out with ease (cf. DABCO/DMAP-assisted one-pot tritylation–acetylation protocol in CH_2Cl_2 we have reported earlier[13d]) in very high overall yields. Thus, methyl α-D-glucopyranoside could be regioselectively tritylated by treatment with trityl chloride (2 mol equiv) in dichloromethane at rt for 2 h and the generated methyl 6-*O*-trityl-α-D-glucopyranoside was acetylated in the same pot by reacting with Ac_2O (1.2 mol equiv/OH group) in the presence of DABCO (1 mol equiv) for 40 min to obtain, after chromatographic purification, the desired methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranoside in 88% yield.[15] The acetylation of amino sugars (Table 1, entries 12 and 17), which usually requires up to 24 h by the conventional method in pyridine, could also be achieved appreciably faster (in 2–4 h) using the current method.

A comparative evaluation of some of the literature methods, the classical pyridine-mediated reaction along with a few of the more recently reported methods comprising of acidic, basic as well as neutral promoters, was then carried out on three representative sugar substrates and the results are summarized in Table 2. In all cases studied the DABCO-mediated reaction was proved substantially superior in terms of one or more of the parameters such as the reaction time, requirement of a solvent for the reaction, reaction yield and the convenience of carrying out the reaction (e.g., the reaction temp, see Table 2).

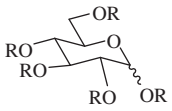
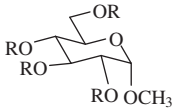
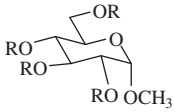
Further, in order to establish the general applicability of the method to other types of organic compounds, the work was

Table 2
Comparison of the current method with some of the reported methods[a]

Compound structure: R = H → R = Ac	Catalyst	Reaction		Refs.
		Time (min)	Yield (%)	
	$LiClO_4$	50	93	19
	TsOH[b]	10	90	24
	Pyridine	8	96	3
	DABCO	4	96	—
	$HClO_4$	22	—[e]	8a,8b
	H_2SO_4	3	—[e]	3
	Pyridine[d]	6	95	—
	DABCO	3.5	94	
[c] 	I_2	3.0	40[f]	6
	$Cu(OTf)_2$	5	80	12d
	Al_2O_3	12	30[g]	25
	Pyridine[d]	0.75	95	3
	Imidazole[b]	2	98	5
	DABCO	0.3	98	—

[a] Substrate (1 g) with Ac_2O, 1.2 mol equiv per OH/NH_2 group and DABCO, 1.0 mol equiv, were used for the reaction at rt under neat condition.
[b] Acetonitrile was used as the solvent.
[c] The starting sugar used was hydrochloride salt.
[d] Pyridine was used as the solvent.
[e] Per-O-acetylation does not take place.
[f] The remaining was degraded product to avoid degradation the reaction needs to be held at icebath temp or below.
[g] The reaction not complete.

Table 3
DABCO-mediated acylation/alkylation/silylation of carbohydrates and their derivatives[a]

Sugar substrate	Reagent, RCl	Reaction		Refs.
		Time (min)	Yield (%)	
 R = H → R = Bz	BzCl (Under neat condition)[b]	1.5	93	18
 R = H → R = TBDMS	TBDMSCl (CH_2Cl_2)	2	92	26
 R = H → R = Tr	TrCl (CH_2Cl_2)	3.5	98	13d

[a] Substrate (1.0 g) with RCl, 1.2 mol equiv per OH group and DABCO, 1.0 mol equiv in CH_2Cl_2 (20 mL), were used for the reaction at rt.
[b] No solvent was used.

extended to a few of the representative non-carbohydrate hydroxylic substrates [aryl (phenol, Table 1, entry 20), aryl-substituted alkyl (benzyl alcohol, Table 1, entry 21), alkyl (octanol, Table 1, entry 22), substituted/hindered/chiral (menthol, Table 1, entry 23) and steroidal (cholesterol, Table 1, entry 24)] and it was found that acetylation can be carried out with equal ease and efficiency in all of the cases (Table 1, entries 20–24).

It may be pointed out that the use of acetic anhydride as an acyl donor reagent in the acetylation reactions under neat conditions described above, in particular in the case of per-O-acetylation of unprotected carbohydrates, was found to be well suited as the acetic acid formed as a by-product in the reaction served as an excellent solvent for the acetylated product. Moreover it was also found to be commercially much cheaper than acetyl chloride, a popular alternative for the purpose, besides the fact that it is also more stable and easier to handle as a reagent compared to the latter.

Finally, the reaction was also proved equally applicable to the synthesis of per-O-benzoylated sugar derivatives such as penta-*O*-benzoyl-α-D-glucopyranose (Table 3, entry 1) using BzCl as the acyl donor reagent and to the regioselective 6-O-silylation of aldohexopyranosides using TBDMSCl as the silyl donor reagent (Table 3, entry 2). In the case of benzoylation of sugars under neat condition the use of the acid chloride (BzCl), being a liquid, as the acyl donor reagent was proved more convenient compared to the solid benzoic anhydride, the alternative reagent for the purpose. Likewise, TBDMSCl being a solid, the reaction was carried out in a solvent and CH_2Cl_2 (in place of the conventional solvents such as pyridine and DMF) was found to serve the purpose well. DABCO is also a highly efficient promoter of regioselective 6-O-tritylation of hexosides as reported earlier (Table 3, entry 3).[13d]

In conclusion, a simple and convenient method has been developed for the acetylation of a variety of carbohydrates and their derivatives under solvent-free conditions. The method is highly efficient and yields the desired product in high yields under mild reaction conditions within short reaction times. The method is characterized by its ease of operation, and the use of a relatively less-toxic, easily available and inexpensive catalyst. Perbenzoylation of sugars, regioselective tritylation/silylation of hexosides followed by, if desired, global acetylation of the remaining hydroxyl groups on them in the same pot are some of the other reactions possible in high overall yield using DABCO as a convenient promoter.

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14. *Typical procedure:* Acetylation of methyl α-D-glucopyranoside. DABCO (1.0 mol equiv) was added to a suspension of the sugar (10.0 g, 51.5 mmol) in Ac_2O (1.2 mol equiv per OH group) and the mixture was stirred at rt. After completion of the reaction (TLC, eluent, EtOAc:*n*-Hex, 2:3) the mixture was poured onto crushed ice and was stirred for a few min when precipitation of the desired methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside took place along with dissolution of DABCO in water (the latter indicated by TLC and viewing the spot in an iodine chamber). The product was isolated by filtration at the pump followed by washing with ice-cold water and drying. It was pure enough for direct further use. Yield, 18.3 g, 98%. An analytically pure sample was obtained by recrystallization from 95% ethanol.
It may be noted that addition of DABCO and stirring lead to warming up of the reaction mixture. In reactions carried out on 10–20 g scale this is advantageous in that considerable rate enhancement can be obtained in such cases. However in reactions on a much larger scale (50–100 g and above) the addition of DABCO should preferably be carried out portion-wise to keep the reaction mixture from getting over heated.
15. *Typical procedure:* One-pot sequential tritylation–acetylation of methyl-α-D-glucopyranoside. Methyl-α-D-glucopyranoside (10.0 g, 51.5 mmol) was suspended in anhydrous methylene chloride (100 ml) and DABCO (2 mol equiv) followed by TrCl (2 mol equiv) were added. The mixture was then stirred at rt until the reaction was complete (TLC, eluent, CH_2Cl_2:MeOH, 9:1). Complete dissolution of the sugar occurred upon completion of the reaction. Ac_2O (1.2 mol equiv per OH group) and DABCO (1.2 mol equiv) were then added to the reaction mixture and the stirring was continued at rt. When the acetylation was complete (TLC, eluent, EtOAc:*n*-Hex, 1:3) the mixture was diluted with CH_2Cl_2 and was washed with cold water in a separating funnel. The organic layer was dried (Na_2SO_4), concentrated to dryness under reduced pressure and was purified by chromatography on silica gel (eluent, EtOAc:*n*-Hex, 1:9) to yield pure methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranaoside. Yield, 25.5 g, 88%.
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