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Bismuth(III) salts as convenient and efficient catalysts for the selective acetylation and benzoylation of alcohols and phenols

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Abstract—Efficient acetylation and benzoylation of alcohols and phenols with acetic and benzoic anhydrides have been carried out under catalysis of bismuth(III) salts including $BiCl_3$, $Bi(TFA)_3$ and $Bi(OTf)_3$. Selective acetylation and benzoylation of alcohols in the presence of phenols is an additional advantage of this procedure.

The protection of hydroxyl groups of alcohols and phenols by the formation of esters is one of the most important and widely used transformations in organic chemistry.[1] Protection of such functional groups is often necessary during the course of various transformations in a synthetic sequence, especially in the construction of polyfunctional molecules such as nucleosides, carbohydrates, steroids and natural products. In general, acylations take place by treatment of alcohols and phenols with acid anhydrides or acid chlorides in the presence of tertiary amines such as triethylamine and pyridine.[2] In addition, 4-(dimethylamino)pyridine (DMAP),[3] *N,N,N′,N′*-tetramethylethylenediamine (TMEDA),[4] tributylphosphine,[5] iodine,[6] *p*-toluenesulfonic acid,[7] alumina,[8] zinc chloride,[9] cobalt chloride,[10] montmorillonite K-10 and KSF,[11] scandium triflate,[12] sulfamic acid,[13] indium triflate,[14] copper triflate,[15] tantalum chloride,[16] trimethylsilyl triflate,[17] magnesium bromide,[18] bismuth triflate,[19] silica gel-supported sodium hydrogen sulfate,[20] Pseudomonas cepacia PS lipase adsorbed on celite[21] and twisted amides[22] have also been applied for the acylation of alcohols and phenols. However, some of these methods are not entirely satisfactory: triethylamine and pyridine have unpleasant odors and are not so easy to remove; tributylphosphine is an irritant which is highly flammable and expensive; indium and scandium triflates are expensive catalysts; magnesium bromide suffers from low yields of the products and long reaction times. Therefore, introduction of new methods and catalysts for the preparation of esters is still in demand.

The applications of bismuth compounds to organic transformations have been extensively investigated.[19,23] Recently, we introduced $BiCl_3$ as an efficient catalyst for the conversion of oxiranes to thiiranes,[24] deprotection of 1,1-diacetates,[25] and alcoholysis, hydrolysis and acetolysis of epoxides.[26] In continuation of our work on Bi(III) catalysis, we now report a simple and efficient method for the acetylation and benzoylation of alcohols and phenols catalyzed by $BiCl_3$, $Bi(TFA)_3$ and $Bi(OTf)_3$ (Scheme 1).

As shown in Table 1, primary and secondary alcohols and phenols are acetylated with acetic anhydride in excellent yields under catalysis of $BiCl_3$, $Bi(TFA)_3$ and $Bi(OTf)_3$ (entries 1–23). Dihydroxyl compounds are converted into the corresponding diacetates efficiently (entries 24–26). Tertiary alcohols such as triphenylmethanol (entry 27) remained unchanged when the reaction was catalyzed by $BiCl_3$ and $Bi(TFA)_3$, but in the presence of $Bi(OTf)_3$ the corresponding acetate was obtained in 80% yield. However, *tert*-butyl alcohol (entry 28) acetylated in excellent yield in the presence of these catalysts.

In order to extend the scope of these catalysts further, the benzoylation of alcohols and phenols with benzoic anhydride, a less reactive anhydride, was also investigated. The results of this investigation are shown in Table 2. Treatment of a series of alcohols and phenols with benzoic anhydride in the presence of catalytic amounts of $BiCl_3$, $Bi(TFA)_3$ and $Bi(OTf)_3$ provided the corresponding benzoates in excellent yields (entries 1–23). Dihydroxyl compounds such as catechol, resorcinol and hydroquinone are transformed to their dibenzoates efficiently (entries 24–26). Tertiary alcohols such as triphenylmethanol and *tert*-butyl alcohol remained intact or benzoylated in poor yields (entries 27 and 28). The experimental results show that $Bi(OTf)_3$ is more reactive and works better than the two

$$\mathrm{ROH + (R'CO)_2O \xrightarrow[\text{CH}_3\text{CN, rt or reflux}]{\text{Bi(III) salts}} R'CO_2R}$$

$$\mathrm{R' = CH_3, Ph}$$

Scheme 1.

Keywords: acylation; alcohols; phenols; catalysts; bismuth compounds.

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Table 1. Acetylation of alcohols and phenols catalyzed by Bi(III) salts

Run	Substrate	Product[a]	Yield (%)[b]/Condition/Time (min)		
			$BiCl_3$	$Bi(TFA)_3$	$Bi(OTf)_3$
1	Benzyl alcohol	Benzyl acetate	98/rt/35	96/rt/60	99/rt/5
2	2-Methoxybenzyl alcohol	2-Methoxybenzyl acetate	97/rt/60	98/rt/90	99/rt/5
3	3-Methoxybenzyl alcohol	3-Methoxybenzyl acetate	98/rt/55	97/rt/90	98/rt/5
4	2-Nitrobenzyl alcohol	2-Nitrobenzyl acetate	94/rt/180	95/rt/180	97/rt/5
5	3-Nitrobenzyl alcohol	3-Nitrobenzyl acetate	95/rt/75	95/rt/120	98/rt/5
6	4-Nitrobenzyl alcohol	4-Nitrobenzyl acetate	95/rt/30	90/rt/60	98/rt/5
7	4-Chlorobenzyl alcohol	4-Chlorobenzyl acetate	98/rt/50	97/rt/60	98/rt/5
8	4-Bromobenzyl alcohol	4-Bromobenzyl acetate	90/rt/60	95/rt/105	99/rt/5
9	Benzoin	Benzoin acetate	98/reflux/35	95/rt/60	99/rt/5
10	Cinnamyl alcohol	Cinnamyl acetate	90/reflux/60	85/rt/135	97/rt/5
11	2-Phenylethanol	2-Phenylethyl acetate	98/rt/60	98/rt/60	99/rt/5
12	1-Heptanol	1-Heptyl acetate	98/rt/45	98/rt/60	99/rt/5
13	1-Octanol	1-Octyl acetate	97/rt/45	95/rt/60	98/rt/5
14	2-Octanol	2-Octyl acetate	95/rt/20	93/rt/40	99/rt/5
15	Cyclohexanol	Cyclohexyl acetate	94/rt/35	90/rt/60	98/rt/15
16	(−)-Methanol	(−)-Menthyl acetate	94/reflux/20	93/rt/25	95/rt/20
17	Phenol	Phenyl acetate	97/reflux/50	90/reflux/120	98/rt/5
18	2-Nitrophenol	2-Nitrophenyl acetate	92/reflux/120	85/reflux/180	94/rt/45
19	4-Nitrophenol	4-Nitrophenyl acetate	96/reflux/60	80/reflux/120	98/rt/5
20	4-Methoxyphenol	4-Methoxyphenyl acetate	97/reflux/35	94/reflux/120	98/rt/5
21	4-Hydroxybenzaldehyde	4-Acetoxybenzaldehyde	80/reflux/90	80/reflux/180	90/rt/60
22	α-Naphthol	α-Naphthyl acetate	98/reflux/65	95/reflux/120	99/rt/5
23	β-Naphthol	β-Naphthyl acetate	95/reflux/90	85/reflux/120	98/rt/5
24	Catechol	Benzene-1,2-diyl diacetate	95/reflux/180	95/reflux/90	97/rt/15
25	Resorcinol	Benzene-1,3-diyl diacetate	94/reflux/65	90/reflux/45	98/rt/10
26	Hydroquinone	Benzene-1,4-diyl diacetate	94/reflux/60	85/reflux/60	95/rt/15
27	Triphenylmethanol	Triphenylmethyl acetate	0/reflux/120	0/reflux/120	80/rt/35
28	*tert*-Butyl alcohol	*tert*-Butyl acetate	98/reflux/20	96/reflux/30	98/rt/10

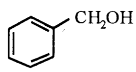
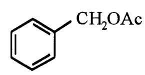
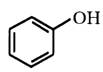
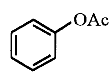
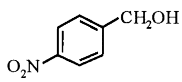
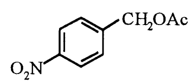
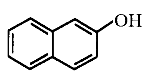
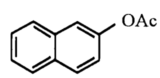
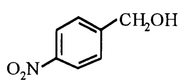
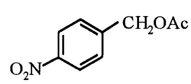
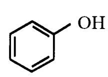
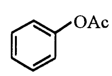
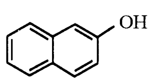
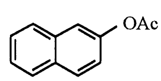
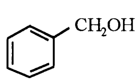
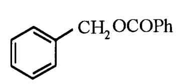
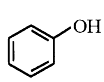
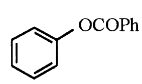
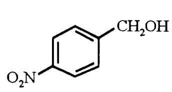
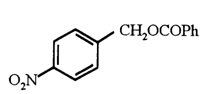
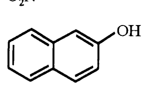
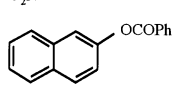
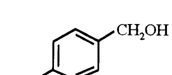
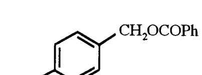
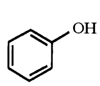
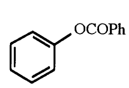
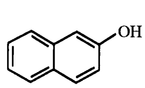
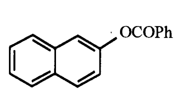
[a] All products were identified by comparison of their physical and spectral data with those of authentic samples.
[b] Isolated yields.

Table 2. Benzoylation of alcohols and phenols catalyzed by Bi(III) salts

Run	Substrate	Product[a]	Yield (%)[b]/Time (min)		
			$BiCl_3$	$Bi(TFA)_3$	$Bi(OTf)_3$
1	Benzyl alcohol	Benzyl benzoate	97/45	95/60	98/30
2	2-Methoxybenzyl alcohol	2-Methoxybenzyl benzoate	90/60	90/80	95/35
3	3-Methoxybenzyl alcohol	3-Methoxybenzyl benzoate	91/60	90/65	99/30
4	2-Nitrobenzyl alcohol	2-Nitrobenzyl benzoate	96/80	91/80	98/30
5	3-Nitrobenzyl alcohol	3-Nitrobenzyl benzoate	97/70	90/70	97/25
6	4-Nitrobenzyl alcohol	4-Nitrobenzyl benzoate	94/80	88/100	99/40
7	4-Chlorobenzyl alcohol	4-Chlorobenzyl benzoate	95/45	94/60	98/30
8	4-Bromobenzyl alcohol	4-Bromobenzyl benzoate	98/40	91/60	99/30
9	Benzoin	Benzoin benzoate	91/60	92/80	99/35
10	Cinnamyl alcohol	Cinnamyl benzoate	95/70	92/75	95/35
11	2-Phenylethanol	2-Phenylethyl benzoate	97/40	94/60	98/25
12	1-Heptanol	1-Heptyl benzoate	94/35	95/60	96/20
13	1-Octanol	1-Octyl benzoate	92/40	94/50	97/25
14	2-Octanol	2-Octyl benzoate	95/45	90/60	98/30
15	Cyclohexanol	Cyclohexyl benzoate	93/60	91/85	94/35
16	(−)-Menthol	(−)-Menthyl benzoate	91/45	90/60	95/30
17	Phenol	Phenyl benzoate	96/120	95/180	98/25
18	2-Nitrophenol	2-Nitrophenyl benzoate	94/180	80/180	95/60
19	4-Nitrophenol	4-Nitrophenyl benzoate	90/120	93/180	95/50
20	4-Methoxyphenol	4-Methoxyphenyl benzoate	93/80	82/180	94/45
21	4-Hydroxybenzaldehyde	4-Benzoyloxybenzaldehyde	94/100	89/120	95/45
22	α-Naphthol	α-Naphthyl benzoate	90/100	83/120	92/45
23	β-Naphthol	β-Naphthyl benzoate	94/90	90/120	95/45
24	Catechol	Benzene-1,2-diyl dibenzoate	91/120	82/180	94/60
25	Resorcinol	Benzene-1,3-diyl dibenzoate	93/100	91/180	95/60
26	Hydroquinone	Benzene-1,4-diyl dibenzoate	97/100	92/120	99/60
27	Triphenylmethanol	Triphenylmethyl benzoate	0/120	0/120	5/120
28	*tert*-Butyl alcohol	*tert*-Butyl benzoate	40/120	10/120	45/80

Reactions were performed in refluxing CH_3CN.
[a] All products were identified by comparison of their physical and spectral data with those of authentic samples.
[b] Isolated yields.

Table 3. Competitive acetylation and benzoylation of alcohols and phenols catalyzed by Bi(III) salts

Run	Substrate	Product	Yield (%) (Condition/Time(min))		
			$BiCl_3$	$Bi(TFA)_3$	$Bi(OTf)_3$
1			95 (rt/40)	95 (rt/60)	100 (rt/5)
			4	0	0
2			95 (reflux/35)	80 (reflux/60)	100 (rt/25)
			5	17	0
3			80 (reflux/45)	90 (reflux/60)	90 (rt/45)
			18	5	0
4	$CH_3(CH_2)_5CH(OH)CH_3$	$CH_3(CH_2)_5CH(OAc)CH_3$	89 (rt/20)	90 (rt/40)	82 (rt/5)
			0	0	12
5			90 (reflux/45)	86 (reflux/60)	95 (reflux/30)
			5	10	5
6			90 (reflux/80)	80 (reflux/100)	94 (reflux/40)
			10	10	5
7			89 (reflux/80)	80 (reflux/100)	93 (reflux/40)
			2	0	5
8	$CH_3(CH_2)_5CH(OH)CH_3$	$CH_3(CH_2)_5CH(OCOPh)CH_3$	80(reflux/45)	85(reflux/60)	90 (reflux/35)
			20	12	10

other catalysts in terms of reaction times, temperature and the yields of the products. It is also noteworthy that bismuth triflate is better when compared with indium and scandium triflates as it is easier to handle and less expensive.

In order to show the selectivity of the described method, we have also investigated the competitive acetylation and benzoylation of alcohols and phenols, and found that alcohols were acetylated and benzoylated selectively in the presence of phenols (Table 3). This may be considered as a useful practical achievement in esterification reactions.

In conclusion, we have developed an efficient and excellent yielding method for the acetylation and benzoylation of alcohols and phenols. In addition, high chemoselectivity, mild reaction conditions, high reaction rates and easy work-up are worthy advantages of this method.

1. Experimental

1.1. General

All of the products were characterized by comparison of their spectral and physical data with those of authentic samples. Yields refer to isolated products. $Bi(TFA)_3$ and $Bi(OTf)_3$ were prepared according to the reported procedures.[27]

1.2. General experimental procedure for acetylation

To a solution of alcohol or phenol (1 mmol) and acetic anhydride (1.5 equiv. for each hydroxyl group of alcohol or phenol) in CH_3CN (3 mL) was added the catalyst (0.1 mmol of $BiCl_3$, 0.05 mmol of $Bi(TFA)_3$ and 0.01 mmol of $Bi(OTf)_3$). The reaction mixture was stirred at room temperature or under reflux conditions for the appropriate time according to Table 1. The progress of the reaction was followed by GLC or TLC. The solvent was evaporated and ether (20 mL) was added. The reaction mixture was washed with 5% aqueous solution of $NaHCO_3$, then with water, and dried with Na_2SO_4. Evaporation of the solvent followed by chromatography on a silica-gel plate or silica-gel column afforded the pure acetate (Table 1).

1.3. General experimental procedure for benzoylation

To a solution of alcohol or phenol (1 mmol) and benzoic anhydride (1.5 equiv. for each hydroxyl group of alcohol or phenol) in CH_3CN (3 mL) was added the catalyst (0.1 mmol of $BiCl_3$, 0.05 mmol of $Bi(TFA)_3$ and 0.01 mmol of $Bi(OTf)_3$). The reaction mixture was stirred under reflux conditions for the appropriate time according to Table 2. The progress of the reaction was followed by GLC or TLC. The solvent was evaporated and ether (20 mL) was added. The reaction mixture was washed with 5% aqueous solution of $NaHCO_3$, then with water, and dried with Na_2SO_4. Evaporation of the solvent followed by chromatography on a silica-gel plate or silica-gel column afforded the pure benzoate (Table 2).

Acknowledgements

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