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Novel quaternary ammoniumboronate salts as selective acylation catalysts

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Abstract

N-boronomethyltrialkylammonium salts were prepared via the reaction of trialkyl amines with α-halomethylboronates. These compounds were utilized as selective catalysts for acetylation of primary alcohols and aldehydes.

Keywords: Iodomethylpinacolboronate; Boronomethylammonium salts; Acetylation; Acylal

1. Introduction

Development of novel catalysts for selective organic transformations is fundamentally an important process for organic synthesis. The catalysts that act on one particular group without affecting the remaining functional groups in a complex molecule are of paramount importance. As a part of our ongoing project involving the synthesis and evaluation of aminoboronic acids and aminoboronates as precursors for biologically important molecules, we have developed several protocols for the efficient preparation of the title compounds. The convenient access and the chemical stability of these novel aminoboronate salts prompted us to investigate the utility of these compounds for selective transformations in organic synthesis as well.

B-alkylpinacolboronates are known to be stable towards air and moisture. Accordingly, we envisioned that the salts derived from halomethylpinacolboronates and tertiary amines should provide stable quaternary ammonium boronates [1,2]. We envisaged that the presence of boronate moiety and quaternary ammonium group should render mild Lewis acidity and hydrophilicity to the salts and hence they could be used as organocatalysts.

2. Results and discussion

We initiated our synthesis with the preparation of iodomethylpinacolboronate **2**. The reaction of *B*-isopropoxypinacolboronate **1** with lithiated CH_2I_2 at −78 °C afforded **2** [3]. The boronate **2** upon treatment with Methyl amine, imidazole, and *N*-methylmorpholine provided the corresponding ammonium boronates **3a–c** in excellent yields (Scheme 1). All these salts are stable white solids and can be handled in air and are freely soluble in water and dichloromethane.

In order to explore the catalytic properties of these reagents, we first undertook the acetylation of alcohols. Traditionally this reaction is performed with acetic anhydride or acetyl chloride in the presence of tertiary amine bases. The reaction also takes place under acidic conditions and excellent progress has been made on the Lewis acid catalyzed acetylations using variety of catalysts [4]. Acetylation of decanol, hexadecanol, and *p*-methoxybenzyl alcohol with acetic anhydride in the presence of the catalyst **3a** took place readily to provide corresponding decylacetate **4a**, hexadecyl acetate **4b** and *p*-methoxybenzylacetate **4c** in excellent yield (entries 1–3, Table 1). The reaction was very slow at room temperature, however heating the reaction at 50 °C for 2 h resulted in the facile conversion of alcohols to the acetates. The catalysts **3b** and **3c** derived from imidazole and *N*-methylmorpholine, also furnished the acetates of the primary alcohols in good yield (entries 4 and 5, Table 1).

Secondary alcohols did not react under these conditions and they failed to undergo acylation even with excess acetic anhy-

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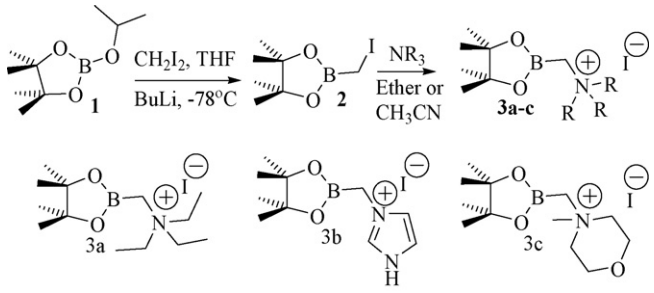
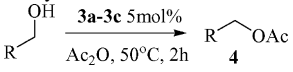


Scheme 1. Preparation of *N*-boronomethyltrialkylammonium salts.

Table 1
Acetylation of alcohols

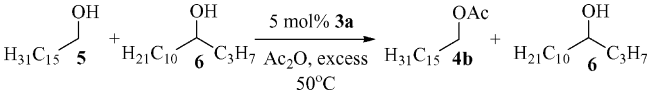


#	Alcohol	Catalyst	Acetate	Yield (%)
1.	1-Decanol	**3a**	**4a**	90
2.	1-Hexadecanol	**3a**	**4b**	92
3.	*p*-Methoxybenzyl alcohol	**3a**	**4c**	89
4.	1-Hexadecanol	**3b**	**4b**	88
5.	1-Hexadecanol	**3c**	**4b**	86
6.	Phenol	**3a**	–	NR
7.	*p*-Toluenethiol	**3a**	–	NR

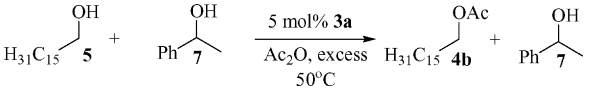
NR: No reaction.

dride and prolonged heating time. When an equimolar mixture of hexadecanol **5** and 4-tetradecanol **6** was heated in the presence of catalyst **3a**, and excess acetic anhydride (10 equivalents), selective formation of 1-hexadecyl acetate was observed along with the quantitative recovery of 4-tetradecanol **6** (Eq. (1)). Even secondary benzylic alcohols **7** (Eq. (2)) and tertiary alcohols **8** (Eq. (3)) did not undergo esterification under these conditions. However, highly activated secondary (allylic/benzylic) alcohol **9** obtained via the Baylis–Hillman reaction [5], underwent acylation under these conditions with the catalyst **3a** (Eq. (4)).

Thiols and phenols remained unreactive even in the presence of excess Ac_2O and prolonged heating (entries 6 and 7, Table 1).



(1)



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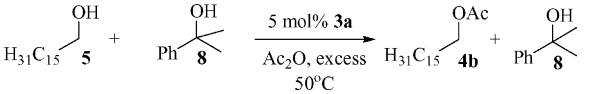
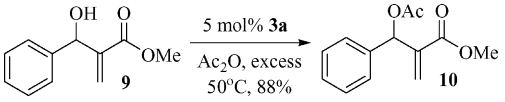
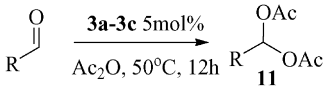


(3)



(4)

Table 2
Acetylation of aldehydes



#	Alcohol	Catalyst	Acetate	Yield (%)
1.	Propionaldehyde	**3a**	**11a**	78
2.	Butyraldehyde	**3a**	**11b**	79
3.	Cyclohexane carboxaldehyde	**3a**	**11c**	80
4.	Benzaldehyde	**3a**	**11d**	85
5.	(*E*)-cinnamaldehyde	**3a**	**11e**	85
6.	Phenylacetaldehyde	**3a**	**11f**	78
7.	Benzaldehyde	**3b**	**11g**	84
8.	Benzaldehyde	**3c**	**11h**	86

Next, we performed the acylation of aldehydes to the corresponding acylals. They are stable and easily removable protecting groups for aldehydes [6,7]. The acylation of several aliphatic, aromatic, and aralkyl aldehydes with Ac_2O in the presence of 5 mol% of the above salts **3a–c** proceeded satisfactorily to yield the product acylals **4a–h** in good yields (entries 1–8, Table 2). Tetrabutylammonium bromide/iodide failed to catalyze the acylation of aldehydes, while alcohols undergo <10% acylation even with excess Ac_2O and heating overnight at 50 °C. The mild Lewis acidity due to the presence of boronate moiety in these salts could be mainly responsible for the product formation.

3. Conclusions

In conclusion, we have synthesized novel *N*-boronomethyl quaternary ammonium salts and have demonstrated the application of these compounds as mild catalysts for the acylation of alcohols and aldehydes. Only primary alcohols and very active secondary alcohols undergo acylation under the reaction conditions. These catalysts are reasonably stable to air and moisture and are freely soluble in both organic and aqueous medium. The mild nature and convenient preparation of the catalysts combined with the easy availability of the chiral boronates and tertiary amines should provide facile access to various optically pure aminoboronate salts, thus further expanding the scope of these compounds for asymmetric catalysis. Further studies in this direction and other applications of these catalysts are in progress.

4. Experimental

*4.1. Preparation of quaternary N-boronomethylammonium salt **3a***

Iodomethylpinacolboronate **2** (2.0 g, 7.7 mmol) was dissolved in diethyl ether (100.0 mL) and triethyl amine (1.6 mL, 11.5 mmol) was added drop wise. The solid quaternary salt precipitated almost immediately. The solid was filtered, washed repeatedly with ether and dried *in vacuo* to obtain 2.6 g (95%) of salt **3a**. ^{1}H NMR ($CDC1_3$, 300 MHz): δ 0.78 (s, 12H), 0.88 (m, 9H), 2.96 (br s, 2H), 3.07 (m, 6H); ^{13}C NMR ($CDCl_3$,

75 MHz): δ 8.7, 24.6, 53.7, 56.5, 85.5; EI-MS: 242.3 [$(M-I)^+$, 100%].

4.2. Preparation of quaternary N-boronomethylammonium salt *3b*

Procedure similar to that of **3a**. Acetonitrile was used as the solvent instead of diethyl ether. Ninety-four percent of catalyst **3b** was obtained. ^{1}H NMR ($CDC1_3$, 300 MHz): δ 1.07 (s, 12H), 3.20 (s, 2H), 6.98 (s, 1H), 7.28 (d, 2H $J = 11.2$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.7, 46.0, 80.3, 121.7, 122.1, 134.0; EI-MS: 209 [$(M-I)^+$, 100%].

4.3. Preparation of quaternary N-boronomethylammonium salt *3c*

Procedure similar to that of **3a**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.12 (s, 12H), 3.11–3.93 (m, 13H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.0, 50.9, 61.0, 61.3, 62.1, 85.9; EI-MS: 242 [$(M-I)^+$, 100%].

4.4. Representative experimental procedure for the acetylation of alcohols

To a solution of alcohol (1 mmol in 1 mL CH_2Cl_2) was added Ac_2O (2 mmol) and salt (**3a**, 0.05 mmol) and heated at 50 °C for 2 h. Upon completion, the reaction mixture was worked up with ether: water and purified by column chromatography to obtain the corresponding acetate.

4.5. Representative experimental procedure for the acetylation of aldehydes

To a solution of aldehyde (1 mmol in 1 mL CH_2Cl_2) was added Ac_2O (2 mmol) and salt (**3a**, 0.05 mmol) and heated at 50 °C for 12 h. Upon completion, the reaction mixture was worked up with ether: water and purified by column chromatography to obtain the corresponding acylal.

Acknowledgements

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