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Acylation of alcohols catalyzed by using 1,3-dibromo-5,5-dimethylhydentoin or trichloroisocyanuric acid

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Abstract

An efficient method for the acylation of alcohols by using acetic anhydride and a catalytic amounts of 1,3-dibromo-5,5-dimethylhydantoin and/or trichloroisocyanuric acid under mild and heterogeneous conditions at room temperature described in good to excellent yields.

Keywords: 1,3-Dibromo-5,5-dimethylhydantoin; Trichloroisocyanuric acid; Acetylation; Alcohols; Acetic anhydrides; Esterification; Heterogeneous conditions

1. Introduction

The acylation of alcohols is an important and frequently used transformation in organic synthesis. The ester moiety is a common functional group in polymers, drugs, and biologically relevant compounds. In addition, the ester functionality serves as a protecting group for alcohols [1], among the various protecting groups which have been reported for alcohols, acetyl is the most common protecting group for this purpose because acetylation of alcohols is very easy under acidic condition, on the other way; hydrolysis of acetates will be occurred quantitative under mild alkaline conditions [2].

Acetyl chloride and acetic anhydride are generally used as the acetylating agents in the presence of an activator [2–6]. A variety of reagents, such as $RuCl_3$ [7], $InCl_3$ [3], NBS [5], $PdCl_2/CuCl_2$ [8], DMAP [9], $Sc(OTf)_3$ [10], $Cu(OTf)_2$ [11], $BiOClO_4 \cdot xH_2O$ [12], Fe_2O_3 [13], $Mg(ClO_4)_2$[14], Al_2O_3 [15], *N*-heterocyclic carbenes [16], Nafion-H [17],$CoCl_2$ [18], TMSOTf [19], $Al(HSO_4)_3$ [20], yttria–zirconia [21], $LiClO_4$ [22], chloride-tethering silica [23] and silica sulfuric acid [24] catalyzed acylation of alcohols.

Despite a number of methods that currently available, new and efficient methods are still in strong demand. On the other hand, these acylation methodologies suffer from disadvantages, such as stringent and complicated conditions, use of hazardous and costly materials, and water sensitive catalysts etc.

2. Results and discussion

In continuation of our studies in this regard [25], and application of *N*-halo reagents in organic reactions, we have found that trichloroisocyanuric acid (TCCA) [26], and 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) [27], as a cheap commercially available reagents used primarily as a disinfectant and deodorant, have found little application in organic chemistry [28]. Therefore, we wish to report a protocol for the efficient conversion of alcohols into their corresponding acetates with acetic anhydride and a catalytic amount of 1,3-dibromo-5,5-dimethylhydantoin (**I**) or trichloroisocyanuric acid (**II**) (Scheme 1).

Different types of alcohols **1** were subjected to the acylation reaction using acetic anhydride and catalytic amount of DBDMH (**I**) or TCCA (**I**) in dichloromethane at room temperature with good to excellent yields (Scheme 2 and Table 1).

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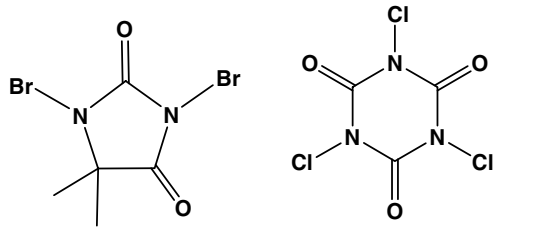


Scheme 1.

It was observed that reaction proceed more rapidly and effectively with 1,3-dibromo-5,5-dimethylhydantoin than trichloroisocyanuric acid. Therefore, catalyst **I** is more active than catalyst **I** (Table 1). Also, the corresponding acetates were obtained rapidly with unhindered alcohols than hindered alcohols.

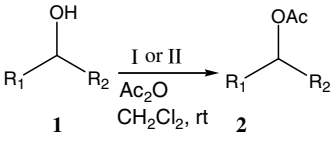
For showing the selectivity of the described system, a competitive reaction was designed. A mixture of an equal amounts of acetic anhydride, benzoic anhydride and benzyl alcohol in the presence of one of the reagents, i.e., TCCA (**I**) or DBDMH (**II**) was subjected to acylation of benzyl alcohol (Scheme 3). In this reaction benzyl acetate obtained solely with 100% conversion so that we do not observe any benzoylated product.

In order to learn the catalytic activity of DBDMH and TCCA, we compared our obtained results for the acylation of menthol with the best of the well-known data from literature (Table 2) as shown in Table 2. The advantages or the characteristic aspects of the described method in this communication in comparison with other previously reported catalysts are: the reaction occurs at room temperature [14,18,9,10,19] with good to high yield of the products [9,19], and using a stoichiometric amounts of Ac_2O [17]. The other advantages of these catalysts (DBDMH and TCCA) are, the low cost [10,19] no moisture sensitivity

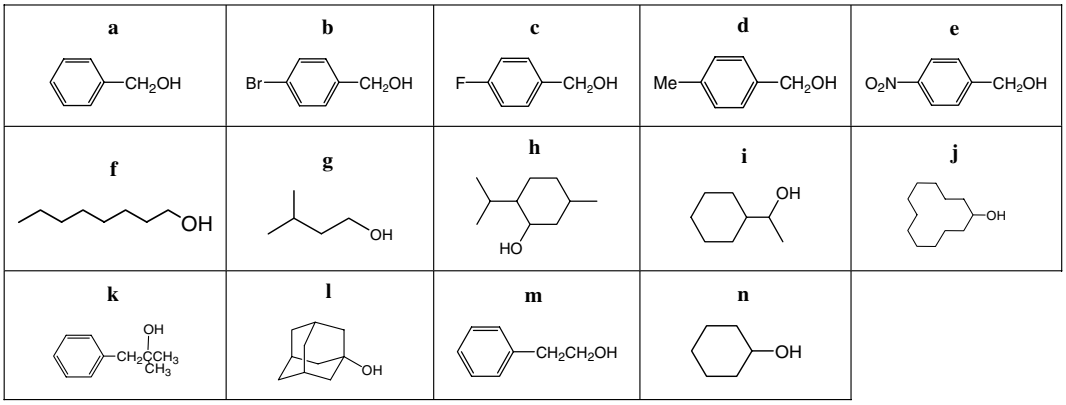
Table 1
Acylation of alcohols using Ac_2O catalyzed with DBDMH (**I**) or TCCA (**II**) in dichloromethane at room temperature

Entry	Substrate	Product	Substrate:Ac_2O:**I**:**II**/mmol	Time (h)	Yield (%)[a]
1	1a	2a	1:2:–: 0.05	7.5	97
2	1a	2a	1:1.5: 0.05:–	2	95
3	1b	2b	1:2:–:0.05	7.25	98
4	1b	2b	1:2:0.05:–	2	95
5	1c	2c	1:3:–:0.1	8	70[b]
6	1c	2c	1:2:0.05:–	1.75	93
7	1d	2d	1:2:–:0.05	7	97
8	1d	2d	1:2:0.05:–	1	94
9	1e	2e	1:10:–:0.15	30	28[b]
10	1e	2e	1:5:0.15:–	16.5	90
11	1f	2f	1:3:–:0.1	26	50[b]
12	1f	2f	1:2:0.05:–	8	91
13	1g	2g	1:3:–:0.1	20	82[b]
14	1g	2g	1:3:0.1:–	12	90
15	1h	2h	1:5:–:0.1	20	60[b]
16	1h	2h	1:3:0.1:–	10	96
17	1i	2i	1:3.5:–:0.1	20	65[b]
18	1i	2i	1:3:0.1:–	8	80
19	1j	2j	1:5:–:0.1	20	75[b]
20	1j	2j	1:5:0.1:–	18	90
21	1k	2k	1:10:–:0.15	48	Trace
22	1k	2k	1:5:0.1:–	38	90
23	1l	2l	1:10:–:0.15	48	Trace
24	1l	2l	1:5:0.1:–	38	95
25	1m	2m	1:5:–:0.1	30	90[b]
26	1m	2m	1:1.5:0.1:–	4	92
27	1n	2n	1:5:–:0.1	17.5	80[b]
28	1n	2n	1:4:0.05:–	10	87

[a] Isolated yield.
[b] Conversion (determined by ^1H NMR).



$R_1 = R_2$ = Alkyl or Aryl



Scheme 2.