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SHORT COMMUNICATIONS

Mild and Efficient Procedure for Acetylation and Formylation of Alcohols in the Presence of $Mg(HSO_4)_2$*

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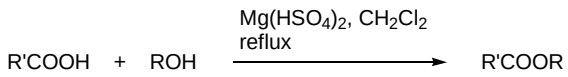
Acetylation and formylation of hydroxy groups are among the most widely used transformations in organic synthesis [1, 2]. Direct esterification of alcohols with carboxylic acids is generally avoided since the equilibrium established between the reactants and the products requires the use of excess initial compounds or removal of water from the reaction mixture to drive the process to completion. Many useful methods for esterification have been reported [3, 4]. Some recently developed procedures utilize organic, inorganic, and organometallic reagents. However, most of these methods are not free from one or more of the following disadvantages: long reaction time, severe conditions, occurrence of side processes, inaccessibility of required reagents, and poor yields of the target products.

Acetylation of alcohols is usually performed with the use of acetic anhydride or acetyl chloride in the presence of a base such as triethylamine or pyridine. The rate of acetylation is known to considerably increase when 4-dimethylaminopyridine is used as cocatalyst [2]. *p*-Toluenesulfonic acid (protic acid) [5] and Lewis acids, e.g., $Cu(OTf)_2$ [6], as well as trimethylsilyl trifluoromethanesulfonate [7] and chlorotrimethylsilane [8], were also efficient as catalysts in acetylation of alcohols.

Formylation is also a very important process in organic chemistry. Although various formylating agents have been reported previously [9, 10], there are still serious limitations to the preparation of formates because of drastic conditions, use of uncommon reagents, formation of undesirable or toxic by-products, application of expensive catalysts for the preparation of formylating agents, and thermal instability of the reagents.

In continuation of our studies on the use of magnesium hydrogen sulfate $Mg(HSO_4)_2$ in organic chemistry [11, 12], in the present communication we describe its application as efficient catalyst for acetylation and formylation of alcohols. All reactions were performed under mild heterogeneous conditions (see table). However, the developed procedure was inefficient in the acetylation and formylation of allyl alcohols (see table, run nos. 6, 15). The reactions are clean, the product yields reach 90%, and the procedure is simple. Further studies on new applications of $Mg(HSO_4)_2$ are now in progress in our laboratories.



For R, see table; R' = H, Me.

General procedure for acetylation and formylation of alcohols in the presence of $Mg(HSO_4)_2$. A mixture of 1 mmol of alcohol, 1 mmol of acetic or ormic acid, and 0.75 mmol of $Mg(HSO_4)_2$ in 5 ml of dry methylene chloride was heated under reflux over a period indicated in table. The progress of reactions was monitored by TLC. When the reaction was complete, the mixture was filtered, and the solid precipitate was washed with 10 ml of methylene chloride. The filtrate was combined with the washings, the solvent was removed, and the residue was purified by column chromatography on silica gel.

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Run no.	Substrate	Reagent	Product[a]	Reaction time, h	Yield,[b] %
1	2-$ClC_6H_4CH_2OH$	AcOH	2-$ClC_6H_4CH_2OAc$	3.5	90
2	4-$BrC_6H_4CH_2OH$	AcOH	4-$BrC_6H_4CH_2OAc$	1.5	85
3	2-$MeC_6H_4CH_2OH$	AcOH	2-$MeC_6H_4CH_2OAc$	1	75
4	$C_6H_5CH(OH)CH_3$	AcOH	$C_6H_5CH(OAc)CH_3$	0.5	87
5	$C_6H_5CH_2CH_2CH_2OH$	AcOH	$C_6H_5CH_2CH_2CH_2OAc$	1.5	85
6	$C_6H_5CH=CHCH_2OH$	AcOH	$C_6H_5CH=CHCH_2OAc$	1	[c]
7	2-$ClC_6H_4CH_2OH$	HCO_2H	2-$ClC_6H_4CH_2OCOH$	5	87
8	4-$BrC_6H_4CH_2OH$	HCO_2H	4-$BrC_6H_4CH_2OCOH$	2	85
9	2-$MeC_6H_4CH_2OH$	HCO_2H	2-$MeC_6H_4CH_2OCOH$	2	70
10	3-$NO_2C_6H_4CH_2OH$	HCO_2H	3-$NO_2C_6H_4CH_2OCOH$	4	75
11	4-$ClC_6H_4CH_2OH$	HCO_2H	4-$ClC_6H_4CH_2OCOH$	8	85
12	$C_6H_5CH(OH)CH_3$	HCO_2H	$C_6H_5CH(OCOH)C_6H_5$	0.5	70
13	$C_6H_5CH_2CH_2CH_2OH$	HCO_2H	$C_6H_5CH_2CH_2CH_2OCOH$	1	80
14	$C_6H_5CH_2CH(OH)CH_3$	HCO_2H	$C_6H_5CH_2CH(OCOH)CH_3$	0.5	83
15	$C_6H_5CH=CHCH_2OH$	HCO_2H	$C_6H_5CH=CHCH_2OCOH$	0.5	[c]

[a] The products were identified by their physical constants, comparison with authentic samples, and IR and NMR spectra.
[b] Isolated product.
[c] Mixture of products.

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