

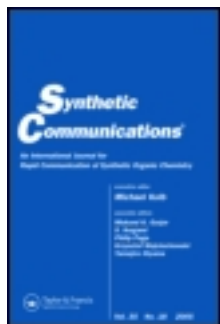
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Catalytic Esterifications of Carboxylic Acids and Alcohols by Sodium Bisulfate Monohydrate

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CATALYTIC ESTERIFICATIONS OF CARBOXYLIC ACIDS AND ALCOHOLS BY SODIUM BISULFATE MONOHYDRATE

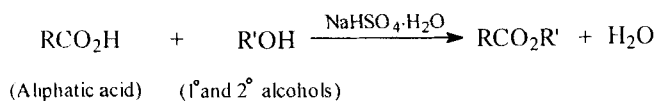
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Abstract: The efficient esterification of primary and secondary alcohols with aliphatic carboxylic acids in the presence of a catalytic amount of sodium bisulfate monohydrate to afford the corresponding esters in high yields.

Esterification of hydroxyl groups is an important and well-established reaction in organic synthesis. The traditional methods use acid and alcohol in the presence of classic mineral acids such as sulfuric acid¹, which are highly corrosive in nature and usually accompanying side reactions such as carbonization, oxidation and dehydration, etc. Several esterification catalysts, which have been found some advantages over the classic acid catalysts, have been reported in literature^{2–8}. Some of these catalysts are also applicable for secondary alcohols, but most require long reaction times and tedious work up.

Recently, the transition metal salts such as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ⁹, $\text{FeSO}_4 \cdot \text{XH}_2\text{O}$ ¹⁰ and $\text{Fe}(\text{ClO}_4)_3(\text{ROH})_6/\text{SiO}_2$ ¹¹ etc. catalyzed esterification have gained wide interest. Herein we wish to report a alkali metal salts, sodium bisulfate monohydrate, catalyzed rapid, convenient and general synthesis of esters from aliphatic carboxylic acids and primary and secondary alcohols (scheme 1).



Scheme 1

Table 1. Esterification of acid with primary and secondary alcohol^a

Entry	Acid	Alcohol	Time(h)	b.p. (°C)	Yields(%) ^b
1	Acetic acid	<i>n</i> -butanol	0.5	124~126	96.2
2	Acetic acid	<i>sec</i> - butanol	1.5	110~112	84.5
3	Acetic acid	<i>iso</i> - butanol	1.0	111~113	92.5
4	Acetic acid	<i>n</i> -pentanol	0.5	146~149	93.6
5	Acetic acid	<i>iso</i> - pentanol	0.5	138~142	85.9
6	Acetic acid	cyclohexanol	1.5 ^c	168~174	84.9
7	Acetic acid	benzyl alcohol	2.0 ^c	202~206	73.7
8	Propanoic acid	<i>n</i> - butanol	0.5	143~145	95.8
9	Propanoic acid	<i>sec</i> - butanol	1.5	130~132	91.5
10	Propanoic acid	<i>iso</i> - butanol	0.5	134~136	95.1
11	Propanoic acid	<i>n</i> - pentanol	0.7	165~169	88.5
12	Propanoic acid	<i>iso</i> - pentanol	0.6	157~161	95.0
13	Chloroacetic acid	ethanol	2.0 ^c	144~146	90.4
14	Chloroacetic acid	<i>iso</i> -propanol	1.5 ^c	146~150	82.9
15	Trichloroacetic acid	ethanol	2.0 ^c	164~168	84.5

^a The molar ratio of acid and alcohol is 1:1, unless otherwise noted

^b Isolated yields

^c Use 30ml cyclohexane as azeotropic entrainer and the molar ratio of acid and alcohol is 1.5:1.0

Esterification of acids and alcohols in the presence of a catalytic amount of NaHSO₄·H₂O is performed under reflux and produces the desired esters in excellent yields (Table 1).

The experimental results show that the esters can be synthesized in large quantities, the reaction condition is mild, the reaction time is short, the yields are excellent and the operation is simple.

Experimental

The esterification of acetic acid with *n*-butanol; Typical Procedure

Place a mixture of 0.4mol of acetic acid, 0.4mol of alcohol, 1.0g of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ and several pieces of boiling chips in a flask, equipped with an automatic water separator carrying a reflux condenser at its upper end. Reflux the mixture on a heating mantle till no more water collects in appreciable amount in the water separator. Filter off the catalyst. The filtrate is washed with 10% sodium bicarbonate solution, brine and dried over anhydrous sodium sulfate, then distilled under the normal pressure to afford the corresponding ester.

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