

Preparation of Alkyl Formates from Corresponding Alcohols using Ethyl Formate Catalyzed by Poly(4-vinylpyridinium tribromide) under Neutral and Solvent-Free Conditions

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The introduction and development of heterogeneous catalysts for fine chemical synthesis has become a major area of research.¹ Also important aspect of clean technology is the use of environment-friendly catalysts.²

Formylation of the hydroxyl group is of great interest because of its importance in organic synthesis, which provides an efficient method for the protection of OH groups. A variety of literature methods were examined for this transformation such as $\text{HCOOH}/\text{SiO}_2$,³ $(\text{NH}_4)_8[\text{CeW}_{10}\text{O}_{36}] \cdot 20\text{H}_2\text{O}$ /ethyl formate,⁴ sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester/ethyl formate,⁵ [bmim]HSO₄/ethyl formate,⁶ silica sulfuric acid/ethyl formate,⁷ $\text{HCOOH}/\text{silica}$ triflate,⁸ $\text{K}_2\text{CO}_3/\text{chloral}$,⁹ $\text{Mg}(\text{HSO}_4)_2/\text{HCOOH}$,¹⁰ 2,2,2-trifluoroethyl formate,¹¹ $\text{PPh}_3/\text{CBr}_4/\text{ethyl formate}$,¹² $\text{K}_5\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$ /ethyl formate.¹³ However most of these procedures suffer from one or more of the following drawbacks: harsh reaction conditions, long reaction times, low yields of products, heavy metal contamination, acidic media (which is not suitable for acid sensitive substrates and side reaction).

Therefore to improve above-mentioned limitation we decided to use non-acidic catalyst and neutral conditions for the preparation of alkyl formates.

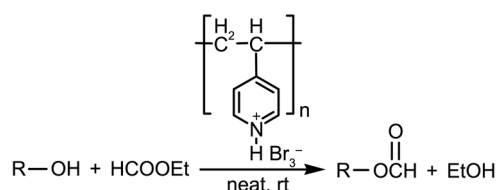
In continuing of our experiments on the application of new reagents or reagent systems in the organic functional group transformations¹⁴⁻²² we became interested to prepare alkyl formates from the corresponding alcohols in the presence of a neutral catalyst. Recently we have introduced a new tribromide reagent (poly(4-vinylpyridinium tribromide)), as

green and none-toxic polymeric reagent (Fig. 1),²³ therefore to investigate the scope and limitation of this reagent we decided to apply poly(4-vinylpyridinium tribromide) as neutral and effective catalyst in the formylation of alcohols with ethyl formate.

Initially, in order to find appropriate conditions 4-fluorobenzyl alcohol was subjected to formylation reaction in different solvents but reaction didn't complete after 24 hours under solvent conditions. The results for solvent screening are summarized in Table 1.

Interestingly we observed that formylation reaction for the 4-fluorobenzyl alcohol completed within 50 min in 91% yield. Eventually, we decide to carry out the formylation reaction in the absence of the solvent (i.e. solvent-free conditions) for the all reactions.

Consequently, a wide variety of alcohols were converted into corresponding alkyl formates using ethyl formate in the presence of a catalytic amount of poly(4-vinylpyridinium tribromide) at room temperature under solvent-free condi-



Scheme 1

Table 1. Formylation of 4-fluorobenzyl alcohol using ethyl formate in the presence of a catalytic amount of poly(4-vinylpyridinium tribromide) at room temperature in the different solvents^a

Entry	Solvent	Time (h)	Yield (%) ^b
1	Acetone	24	38
2	Chloroform	24	31
3	Dichloromethane	24	35
4	<i>n</i> -Hexane	24	58
5	Ethyl acetate	24	71
6	Acetonitrile	24	40
7	No solvent	50 min	91

^aSubstrate : Ethyl formate : Catalyst : solvent for entries 1-6 (1 mmol : 2 mmol : 0.035 g : 5 mL); for entry 7 (1 mmol : 2 mL : 0.035 g : 0 mL).

^bIsolated yield (product purified by short column chromatography).

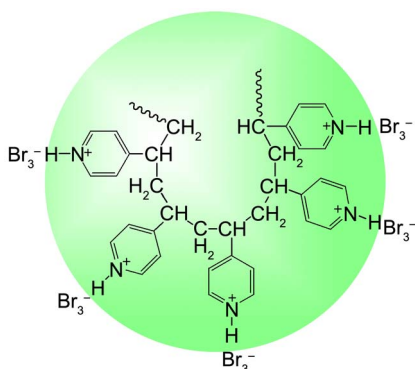
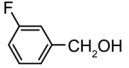
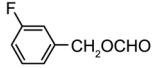
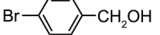
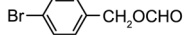
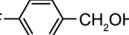
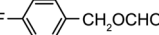
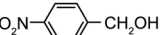
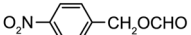
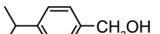
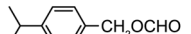
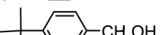
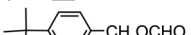
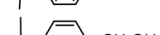



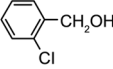
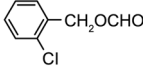
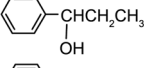
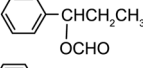
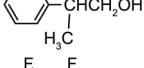
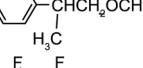
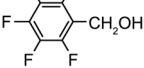
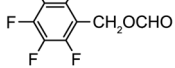
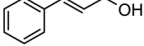
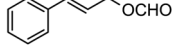
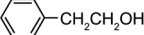
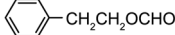


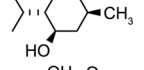
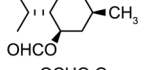
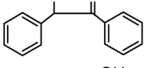
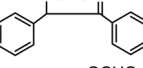
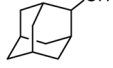
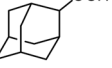
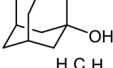
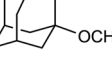
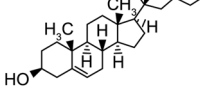
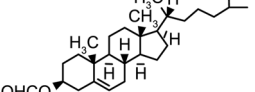

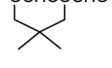
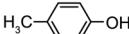
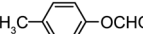


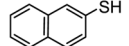
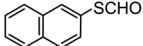
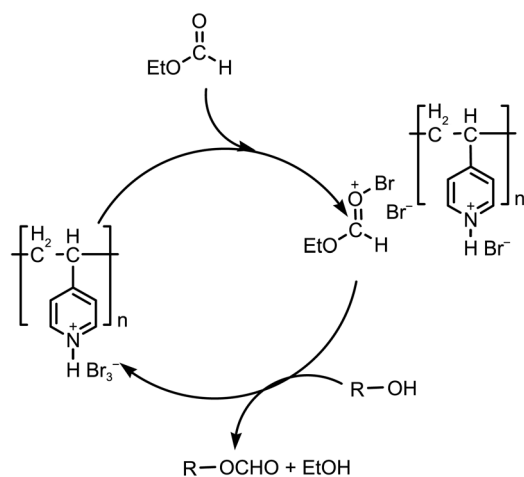


Figure 1. Poly(4-vinylpyridinium tribromide).

Table 2. Formylation of alcohols using ethyl formate **I** in the presence of a catalytic amount of poly(4-vinylpyridinium tribromide) **II** at room temperature under neat conditions

Entry	Substrate	Product	Substrate/Reagents ^a		Time (Min)	Yield (%) ^b
			I	II		
1			2	0.052	60	69
2			2	0.035	40	96
3			2	0.035	50	91
4			2	0.035	90	66
5			2	0.035	50	92
6			2	0.035	45	90
7			2	-	24 h	Trace ^c
8			2	0.035	130	95
9			2	0.035	90	70
10			2	0.035	135	82
11			2	0.035	65	83
12			2	0.052	100	58
13			2	0.035	90	69
14			2	0.035	120	96
15			2	0.035	180	53
16			2	0.035	180	92
17			2	0.052	90	64
18			2	0.035	100	94
19			2	0.035	110	44
20			2	0.035	30 h	89
21			2	0.035	120	76
22			2	0.035	24 h	No R.
23			2	0.035	24 h	- ^d
24			2	0.035	24 h	No R.

^a**I** refers to mL of ethyl formate and **II** refers to gram of the catalyst. ^bIsolated yield (product purified by short column chromatography). ^cReaction proceeds in the absence of the catalyst. ^dReaction didn't complete (conversion is \approx 20%)



tions (Scheme 1). The results of this transformation including molar ration of the reaction components, reaction times and product yields are summarized in Table 2.

Formylation of alcohols selectively proceed under mild conditions and any attempt to prepare formylated phenols and thiols (Table 2, entries 22, 24) was failed. Also formylation of aniline, as representative of amines, only produced $\approx 20\%$ of *N*-formyl aniline.

In order to investigate the catalytic role of poly(4-vinylpyridinium tribromide), 4-*tert*-butylbenzyl alcohol was subjected to formylation reaction in the absence of this compound. Interestingly, only trace conversion of product was observed after 24 h (entry 7), while in the presence of catalyst the same reaction completed within 45 min in 90% yield (Table 2, entry 6).

Suggested mechanism for this transformation is outlined in Scheme 2, based on our previously experience on tribromide^{21,23} and *N*-halo reagents.²⁴⁻²⁷

Poly(4-vinylpyridinium tribromide) acts as a source of Br^+ , which coordinates with oxygen of carbonyl group in ethyl formate to produce active formylating agent. Then a nucleophilic attack of hydroxyl group on the carbonyl group followed by elimination of ethanol gives alkyl formate.

To show the efficiency of the described system in comparison with previously reported procedures in the literature, we compared our obtained results for the preparation of 4-nitrobenzyl formate (as a typical example) with the best of the well-known data from the literature as shown in the Table 3.

In summary, herein we introduced poly(4-vinylpyridinium tribromide) as neutral catalyst for the conversion of alcohols into alkyl formates using ethyl formate. The advantages of this procedure are the avoidance of metallic and acidic catalysts, organic solvents, corrosive and toxic reagents and operational simplicity.

Experimental

General. Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The formylated products were characterized by comparison of their spectral (IR, ^1H NMR, and ^{13}C NMR) and physical data with authentic samples. Poly(4-vinylpyridinium tribromide) was prepared via our previously reported procedure.²³

Formylation of 4-Fluorobenzyl Alcohol using Ethyl Formate Catalyzed by Poly(4-vinylpyridinium tribromide). To a 15 mL round-bottom flask 4-fluorobenzyl alcohol (1 mmol, 0.126 g), ethyl formate (2 mL) and poly(4-vinylpyridinium tribromide), (0.035 g) was added. This mixture was stirred at room temperature for 50 min (the reaction progress was monitored by TLC). After reaction completion, reaction mixture was passed on short column chromatography (packed by silica gel) using dichloromethane as eluent to obtain 4-fluorobenzyl formate in 91% yield (0.140 g).

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Table 3. Comparison of the different methods used for the formylation of 4-nitrobenzyl alcohol using ethyl formate with different catalyst

Entry	Conditions	Catalyst	Time (Min)	Yield (%) ^a	Reference
1	Neat (rt)	Poly(4-vinylpyridinium tribromide)	90	66	This work
2	Neat (rt)	Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester	100	45	5
3	Neat (rt)	$\text{Al}(\text{HSO}_4)_3$	15	89	7
4	Neat (rt)	Silica-bonded <i>N</i> -propyl sulfamic acid	120	35	28
5	Neat (Reflux)	$\text{K}_3\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$	20	92	13
6	Neat (Reflux)	[bmim]HSO ₄	300	50	6

^aIsolated yield.

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