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# $Cl_3CCONH_2/PPh_3$: A Versatile Reagent for Synthesis of Esters

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# $Cl_3CCONH_2/PPh_3$: A Versatile Reagent for Synthesis of Esters

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**Abstract:** $Cl_3CCONH_2/PPh_3$ was a versatile reagent to convert carboxylic acids into their corresponding acid chlorides. This intermediate was clearly confirmed by spectroscopic methods (IR, $^1H$, $^{13}C$ NMR). This one-pot reaction of *in situ* acid chloride generated with various alcohols successfully furnished the corresponding esters in moderate to excellent yields.

**Keywords:** Acid chloride, ester, one-pot conversion, $PPh_3$, trichloroacetamide

## INTRODUCTION

The ester functional group is important in organic and biological chemistry.[1] The preparation of esters from their corresponding carboxylic acids is one of the most fundamental reactions. The general method involves either the use of mineral acid ($H_2SO_4$, HCl, HF, $H_3PO_4$, and $ClSO_2OH$) or Lewis acid catalysts ($BCl_3$, $AlCl_3$, $SiCl_4$, and $FeCl_3$). However, the corrosive nature, extremely slow reaction, and long reaction time are drawbacks. The activation of carboxylic acids has been recognized as another effective alternative.[2] These activation processes can be achieved either by conversion into more reactive functional groups such as acyl halides, anhydrides, acyl azides, and active esters, or *in situ* activation by coupling reagents such as carbodiimides.[3] Acid chloride,

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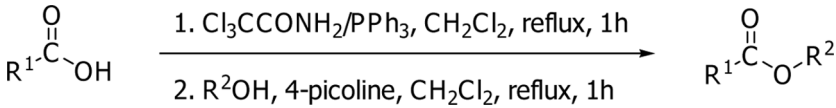
a valuable intermediate, is generally prepared by the reaction of carboxylic acid with common reagents such as $SOCl_2$, $PCl_3$, $POCl_3$, $PCl_5$, and oxalyl chloride.[4] However, such protocols cannot be applied to acid-sensitive compounds because of the vigorous conditions and the formation of strong acids.[5] The application of $PPh_3$ in combination with halogenated reagents such as $CCl_4$,[6] cyanuric chloride,[7] tetramethyl-α-chloroenamine,[8] $Cl_3CCOCCl_3$,[9] *N*-bromo and *N*-iodosaccharins,[10] trichloroisocyanuric acid,[11] and $Br_3CCO_2Et$[12] has been extensively explored for the conversion of alcohols to the corresponding halides or carboxylic acids to their acid halides. Recently, the combination of $Cl_3CCN/PPh_3$ has been found to efficiently convert carboxylic acids into acid chlorides to manipulate amides, esters, and acid anhydrides.[13] These combined reagents have also been reported to convert sulfonic acids into sulfonyl chlorides toward the preparation of sulfonamides.[14] Despite the fact that many reagents and methods have been documented for coupling carboxylic acids and alcohols, certain methods still have their own disadvantages.[15]

More recently, the novel combination of $Cl_3CCONH_2/PPh_3$ has been reported to serve as another efficient coupling reagent for the transformation of alcohols into the corresponding chlorides.[16] and conversion of carboxylic acids into acid chlorides, which were subsequently transformed to the corresponding amides.[17] As an extension to this work and our interest in developing a new protocol for the formation of esters using the combined reagents of $Cl_3CCONH_2/PPh_3$, we report herein a new mild and efficient synthesis for such compounds.

## RESULTS AND DISCUSSION

Interestingly, carboxylic acids can be converted to the corresponding acid chlorides under very mild conditions by simply mixing $PPh_3$ and $Cl_3CCONH_2$ in refluxing $CH_2Cl_2$. Subsequent addition of alcohols in the presence of 4-picoline afforded the corresponding esters in a one-pot procedure (Scheme 1).

PhCOOH–$PPh_3$–$Cl_3CCONH_2$ in a 1:2:2 ratio was utilized in the first step, and the reaction completely proceeded to offer benzoyl chlorides. After 1 h, 4-picoline and 1-octanol were added, and the reaction mixture




***Scheme 1.*** General protocol for the conversion of carboxylic acid to ester.

was stirred in refluxing $CH_2Cl_2$ for another 1 h to afford octyl benzoate in 98% yield (entry 1, Table 1).

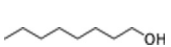
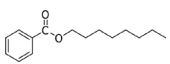
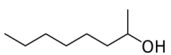
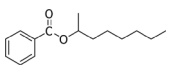
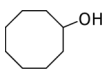
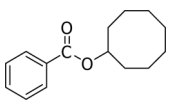
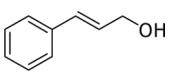
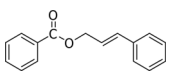
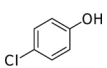
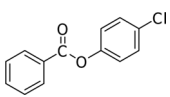
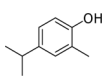
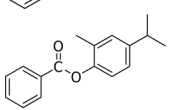
To investigate the generality and scope of the developed method, the reaction was carried out with various structurally diverse alcohols (Table 1).

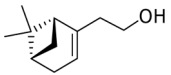
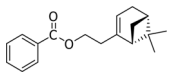
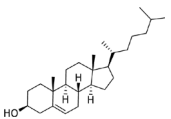
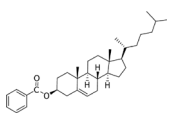
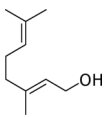
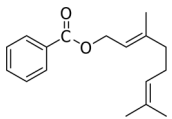
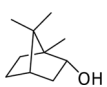
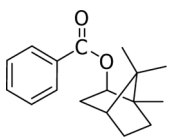
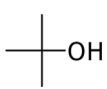
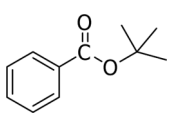
When secondary alcohols such as 2-octanol and cyclooctanol were employed, the corresponding benzoates were afforded in 77 and 66%, respectively (entries 2 and 3). The refluxing time in step 2 for the reaction of 2-octanol was prolonged from 1 to 3 h with the expectation to increase the yield of benzoate ester; the desired benzoate was nevertheless slightly increased. In the case of allylic alcohol as cinnamyl alcohol, the reaction efficiently furnished the target alcohol in good yield (entry 4). In addition, when phenols such as 4-chlorophenol and carvacrol were employed, the desired benzoates were obtained in good yields (75–78%, entries 5 and 6). Moreover, this method was applicable to prepare benzoate esters of (−)-nopol, cholesterol, and geraniol, natural occurring alcohols containing C=C. The reaction proceeded smoothly; C=C was intact (entries 7–9). Additionally, when (−)-borneol was employed to react with benzoic acid, the corresponding ester was obtained in good yield (81%, entry 10). In the case of *t*-butyl alcohol, the desired benzoate was obtained in 53% (entry 11). This may be because of either the steric hindrance of alcohol[13b] or the very high reactivity of *t*-butyl alcohol, causing a rapid dehydration of the alcohol to alkene.[18] Even though the product was achieved in moderate yield, this present method revealed a more superior result than those reported. For example, with the use either of alumina sulfuric acid[19a] or activated basic alumina,[19b] the amount of catalyst relative to the reactants was very large and the reaction period was also very long.

The preparation of esters was then performed using a variety of carboxylic acids to determine the limitations of the method. The results are presented in Table 2.

Treating PPh3/$Cl_3CCONH_2$ with acetic acid and phenethyl alcohol furnished phenethyl acetate in moderate yield (59%, entry 1). To increase the yield of the desired acetate, 2 equivalents of acetic acid were exploited to react with (+)-borneol under the reaction conditions. Unfortunately, the acetate was isolated only in moderate yield similar to the case of phenethyl acetate (entry 2). Treatment of palmitic acid with $Cl_3CCONH_2$ and $PPh_3$, followed by phenethyl alcohol, furnished the formation of the corresponding ester in high yield (74%, entry 3). In the case of sorbic acid, the desired ester was attained in moderate yield (51%, entry 4). Satisfyingly, the reaction of tertiary carboxylic acid such as pivalic acid proceeded smoothly to gain the corresponding ester in high yield (87%, entry 5). However, when the reaction was performed at room

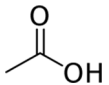
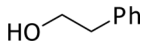
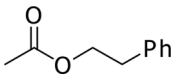
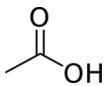
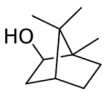
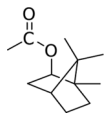
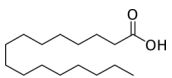
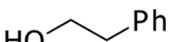
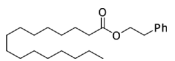
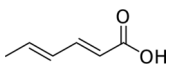
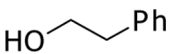
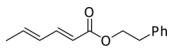
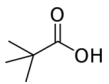
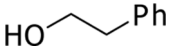
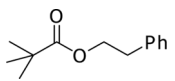
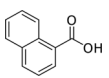
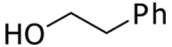
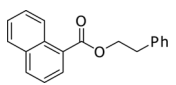
**Table 1.** Effect of alcohols on the synthesis of benzoate esters

| Entry | Alcohol | Benzoate | Isolated yield (%) |
|---|---|---|---|
| 1 |  |  | 98 |
| 2 |  |  | 77 |
| 3 |  |  | 66 |
| 4 |  |  | 90 |
| 5 |  |  | 75 |
| 6 |  |  | 78 |

| | | | |
|---|---|---|---|
| 7 |  |  | 77 |
| 8 |  |  | 81 |
| 9 |  |  | 70 |
| 10 |  |  | 81 |
| 11 |  |  | 53[a] |

[a]3 equiv of *t*-butylalcohol and 6 h for step 2 were used.

**Table 2.** Effect of carboxylic acids on the synthesis of esters

| Entry | Carboxylic acid | Alcohol | Ester | Isolated yield (%) |
|---|---|---|---|---|
| 1 |  |  |  | 59[a] |
| 2 |  |  |  | 67[b] |
| 3 |  |  |  | 74 |
| 4 |  |  |  | 51 |
| 5 |  |  |  | 87(0)[c] |
| 6 |  |  |  | 68 |

[a]1.2 equiv of acetic acid.
[b]2 equiv of acetic acid.
[c]Room temperature (28–30°C) in step 2.

temperature in step 2, no desired ester was attained. Finally, in the case of naphthalic acid, the corresponding ester was afforded in moderate yield (68%, entry 6).

This methodology was further applied to the synthesis of five biologically active esters as presented in Table 3.

The synthesis of benzyl benzoate, an insecticide,[20] was obtained in 85% yield (entry 1). Phenethyl cinnamate and cinnamyl cinnamate, important ingredients of perfume and cosmetics, could be achieved in 98% and 84% yields, respectively (entries 2 and 3). Utilizing this methodology, cholesteryl butyrate and cholesteryl nonanoate, which are widely used for pharmaceutical formulations,[21] could be obtained in high yields (78–89%, entries 4 and 5).

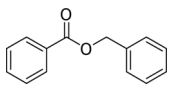
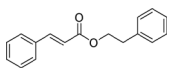
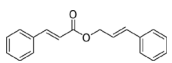
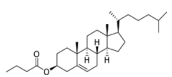
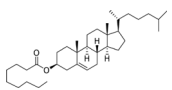
The mechanism of the reaction of carboxylic acids, $PPh_3/CCl_4$, and $PPh_3/Cl_3CCONH_2$ was previously reported to occur via the formation of a reactive intermediate, acid chloride.[6a,16a] To confirm this intermediate of the reaction of carboxylic acid, $PPh_3$, and $Cl_3CCONH_2$, various spectroscopic methods (IR, $^1H$ and $^{13}C$ NMR) were employed.

$Cl_3CCN$ was employed instead of $Cl_3CCONH_2$ to avoid the shade from the C=O peak in IR and $^{13}C$ NMR experiments. The IR spectrum of benzoic acid displayed the strong C=O stretching vibration at $1691\,cm^{-1}$.[22] The strong stretching absorption peak of the C=O was shifted to $1772\,cm^{-1}$ in the case of the reaction mixture derived from the reaction. This strong peak corresponded well to that of commercially available benzoyl chloride.[22] The exploration on the $^{13}C$ NMR spectrum of the reaction mixture revealed a signal of carbonyl carbon at $\delta_C$ 168.4, which coincided well with that of benzoyl chloride, whereas the carbon signal of benzoic acid was detected at $\delta_C$ 172.3.

For the $^1H$ NMR experiment, 4-chlorophenylacetic acid was selected as a model compound. In the absence of $PPh_3$, all starting material was recovered because only the singlet methylene signal at $\delta_H$ 3.50 was displayed. On the other hand, when $PPh_3$ was employed to couple with $Cl_3CCONH_2$, the reaction proceeded to give the new peak at $\delta_H$ 4.18, corresponding to that of phenyl acetyl chloride. (Phenylacetyl chloride was attained from the reaction of 4-chlorophenylacetic acid and $SOCl_2$.) In addition, the reaction was examined using several ratios of $Cl_3CCONH_2$ and $PPh_3$ to compare yields of acid and its acid chloride. When the ratio of $Cl_3CCONH_2$ and $PPh_3$ was increased from 1/1 to 2/2, the yield of the corresponding acid chloride increased from 11 to 72%. In contrast, the yield of the desired product decreased to 57% when the ratio of $Cl_3CCONH_2$ and $PPh_3$ increased to 3/3.

In conclusion, a new protocol utilizing $Cl_3CCONH_2/PPh_3$ for the preparation of ester was introduced. Primary, secondary, and tertiary alcohols smoothly proceeded to the corresponding esters. Moreover, this

**Table 3.** Synthesis of biologically active esters

| Entry | Ester | Isolated yield (%) | Usage |
|---|---|---|---|
| 1 |  | 85 | Insecticide |
| 2 |  | 98 | Perfume and cometic |
| 3 |  | 84 | Cosmetic and drug |
| 4 |  | 78[a] | Cosmetic and pharmaceutical formulation |
| 5 |  | 89[a] | Cosmetic and pharmaceutical formulation |

[a]Step 2 for 3 h.

procedure has proven to be suitable for the synthesis of tertiary carboxylic acid and biologically active esters. IR, $^1H$ NMR, and $^{13}C$ NMR studies strongly endorse the presence of acid chloride as the reactive intermediate.

## EXPERIMENTAL

A typical experimental procedure is as follows: $Ph_3P$ (6 mmol, 1.57 g, 2 equiv) in $CH_2Cl_2$ (3 mL) was added to a mixture of carboxylic acid (3 mmol, 1 equiv) and $Cl_3CCONH_2$ (6 mmol, 2 equiv) in refluxing $CH_2Cl_2$ (3 mL). The mixture was stirred for 1 h. A mixture of alcohol (3 mmol, 1 equiv) and 4-picoline (9 mmol, 3 equiv) was added to this mixture. The reaction mixture was stirred in refluxing $CH_2Cl_2$ for another 1 h and followed by thin-layer chromatography (TLC). When the reaction was completed, the organic layer was washed with 10% HCl and saturated $NaHCO_3$, dried over anhydrous $Na_2SO_4$, and evaporated in vacuo. The mixture was separated with a silica-gel column, eluting with hexane/EtOAc (9:1). Purification by recrystallization with a mixture of $CH_2Cl_2$ and hexane or another appropriate solvent was conducted to achieve the desired ester products. The identities of all isolated products were compared with commercially available acetates and those reported in previous literature.[23]

### Procedure for IR and $^{13}C$ NMR Experiments

The reaction mixture of benzoic acid (1 mmol, 122.2 mg, 1 equiv), $Cl_3CCN$ (2 mmol, 0.20 mL, 2 equiv), and $PPh_3$ (2 mmol, 526.0 mg, 2 equiv) was stirred in refluxing $CH_2Cl_2$ for 1 h. The reaction was then ceased by evaporating all reaction mixture in vacuo. $PPh_3$ and $O{=}PPh_3$ were separated from the reaction mixture by filtration through Celite®, eluting with *n*-hexane. The mother liquor was evaporated in vacuo, and the crude mixture was then characterized by the presence of benzoyl chloride using spectroscopic methods. IR (neat), $cm^{-1}$: 1772. $^{13}C$ NMR $\delta$ (ppm): 168.4.

### Procedure for $^1H$ NMR Experiment

The reaction mixture of 4-chlorophenylacetic acid (0.25 mmol, 34.0 mg, 1 equiv), $Cl_3CCONH_2$ (0.50 mmol, 81.2 mg, 2 equiv), and $PPh_3$ (0.50 mmol, 131.2 mg, 2 equiv) was stirred in $CH_2Cl_2$ at room temperature for 20 min. The reaction mixture was then subjected to the $^1H$ NMR

experiments. The shift of the singlet methylene signal of 4-chlorophenylacetic acid and its chloride were manifestly observed, and yield (%) was determined by $^1$H NMR technique utilizing toluene as the internal standard. For 4-chlorophenylacetyl chloride, $^1$H NMR δ (ppm) 4.18 (2H, s, $CH_2CO_2H$).

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