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# Selective Monoesterification of Symmetrical Diols Using Resin-Bound Triphenylphosphine

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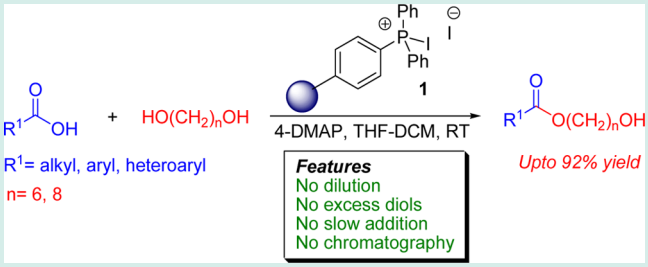
Supporting Information

**ABSTRACT:** Coupling reactions to make esters and amides are among the most widely used organic transformations. We report efficient procedures for amide bond formation and for the monoesterification of symmetrical diols in excellent yields without any requirement for high dilution or slow addition using resin-bound triarylphosphonium iodide. Easy purification, low moisture sensitivity, and good to excellent yields of the products are the major advantages of this protocol.




**KEYWORDS:** *resin-bound triphenylphosphine, selectivity, monoesterification, amides, symmetrical diols, 4-DMAP*

Solid-phase organic synthesis (SPOS) continues to evolve as a means to create and modify compound libraries via combinatorial chemistry.[1] The important advantages of solid-phase synthesis include purification of products by simple filtration of the polymer matrix, easy handling, low moisture susceptibility, minimum side reaction, and recyclability of the polymer matrix for repeated use.[2] Resin-bound triphenylphosphine is a good example[3] because it avoids many of the problems common to the use of $PPh_3$ in solution, such as the removal of excess triphenylphosphine, the formation of phosphine complexes, and the difficulty in removing byproduct triphenylphosphine oxide.[4] Moreover, for the reactions where resin-bound triphenylphosphine acts as an oxygen-acceptor, recycling by reduction of triphenylphosphine oxide with trichlorosilane is convenient.[5]

Carboxylic acid esters and amides are important functional groups, and so many synthetic methods have been reported.[6] Among the mildest of these include the use of hypervalent iodine,[7] *O*-alkylisoureas,[8] DEAD/$Ph_3P$,[9] organocatalytic Mitsunobu reactions,[10] Yamaguchi conditions (TCBC, DIPEA, DMAP),[11] DIC/DMAP,[12] ethyl 2-cyano-2-(4-nitrophenylsulfonyloxyimino)-acetate,[13] $HClO_4$–$SiO_2$,[14] and dodecylbenzenesulfonic acid (DBSA).[15] In addition to some practical disadvantages, many of these methods are unable to discriminate between multiple nucleophilic sites, and thus it remains a challenge to reliably prepare monoesters from di- or polyhydroxylated substrates.

Recently, Robles et al.[16] reported mild methods of esterification using Gregg-Samuelson-type conditions.[17] Manna et al.[18] also reported a chemoselective esterification using triphenylphosphine, $I_2$, and catalytic amount of Zn $(OTf)_2$. While attractive in their selectivity and mild nature, the use of soluble $PPh_3$ leads to the process disadvantages noted above. We report here that the use of solid-phase triphenylphosphine makes for a superior esterification method with useful application to diols.

Stimulated by our previous observations of useful catalytic transformations mediated by resin-bound triphenylphosphine and iodine,[19] we investigated the use of a resin-bound triphenylphosphine-$I_2$ complex (**1**) for the synthesis of esters

**Scheme 1. Formation and Use of Reagent 1**

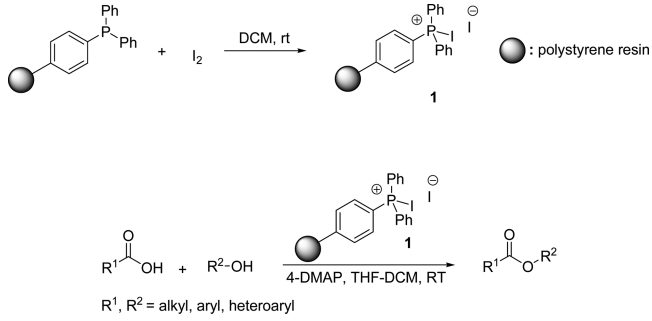
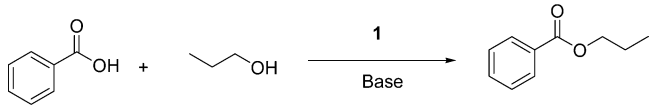



**Table 1. Screening of Base for Esterification Reaction**[a]




| entry | base | time (min) | yield (%)[b] |
|---|---|---|---|
| 1 | pyridine | 45 | 58 |
| 2 | imidazole | 45 | 68 |
| 3 | $K_2CO_3$ | 45 | NR |
| 4 | $Et_3N$ | 45 | 51 |
| **5** | **4-DMAP** | **20** | **91** |
| 6 | | 60 | NR |

[a]Reaction condition: carboxylic acid (1 mmol, 1 equiv), alcohol (1 equiv), 4-DMAP (3 equiv), **1** (1.5 equiv), 20 mL of THF-DCM (1:3 v/v mixture), room temperature. [b]Isolated yield. NR: no reaction.

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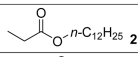
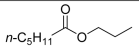
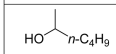
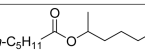
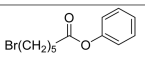
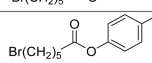
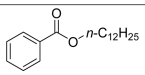
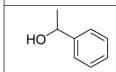
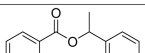
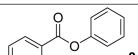
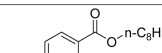
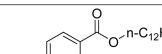
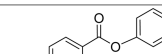
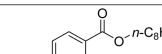
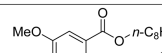
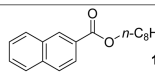
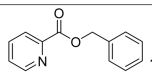
**Table 2. Esterification Reactions under Optimized Conditions[a]**

| Entry | Acid | Alcohol | Product | Time | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | Propionic acid | *n*-$C_{12}H_{25}OH$ |  **2** | 15 | 86 |
| 2 | Hexanoic acid | *n*-$C_3H_7OH$ |  **3** | 15 | 93 |
| 3 | |  |  **4** | 25 | 83 |
| 4 | 6-Bromohexanoic acid | PhOH |  **5** | 25 | 78 |
| 5 | | 4-Me-PhOH |  **6** | 20 | 82 |
| 6 | $PhCO_2H$ | *n*-$C_{12}H_{15}OH$ |  **7** | 25 | 85 |
| 7 | |  |  **8** | 25 | 75 |
| 8 | | PhOH |  **9** | 25 | 80 |
| 9 | 4-Nitrobenzoic acid | *n*-$C_8H_{17}OH$ |  **10** | 15 | 95 |
| 10 | | *n*-$C_{12}H_{25}OH$ |  **11** | 15 | 87 |
| 11 | | 4-Me-PhOH |  **12** | 25 | 79 |
| 12 | 4-Methoxybenzoic acid | *n*-$C_8H_{17}OH$ |  **13** | 40 | 78 |
| 13 | 3,4-Dimethoxybenzoic acid | *n*-$C_8H_{17}OH$ |  **14** | 40 | 65 |
| 14 | 2-Naphthoic acid | *n*-$C_8H_{17}OH$ |  **15** | 40 | 83 |
| 15 | Picolinic acid | $PhCH_2OH$ |  **16** | 20 | 82 |

[a]Reaction condition: carboxylic acid (1 mmol, 1 equiv), alcohol (1 equiv), 4-DMAP (3 equiv), **1** (1.5 equiv), 20 mL of THF-DCM (1:3 v/v mixture), room temperature. [b]Isolated yield.

and amides (Scheme 1). The reagent **1**, was easily prepared by the reaction between resin-bound triphenylphosphine and $I_2$ in anhydrous dichloromethane under nitrogen atmosphere (Scheme 1).[20] It is stable at room temperature (25 °C) and can be stored for long time under vacuum.

A test reaction, the esterification of benzoic acid with 1-propanol in anhydrous THF-DCM (1:3) at room temperature, did not proceed at all after several hours at room temperature in the presence of **1**. The addition of 4-DMAP gave complete reaction within 20 min, allowing for isolation of the desired ester in 91% yield. DMAP was found to be a superior base relative to several others tested (Table 1); the 1:3 THF:DCM mixture in the presence of 3 equiv of base per equivalent of alcohol and acid were found to be optimal conditions (data not shown).

Table 2 shows the results of an investigation of the scope and limitations of the reaction. Desired esters were isolated in good to excellent yield for primary, secondary, and aromatic alcohols. As expected, electron-deficient benzoic acids required shorter reaction times (entries 9−11) than electron-rich cases (entries 12−13). Similarly, phenols were successfully coupled to carboxylic acid giving good yields (entries 4 and 8).

**Scheme 2. Selective Esterification under Optimized Reaction Conditions**

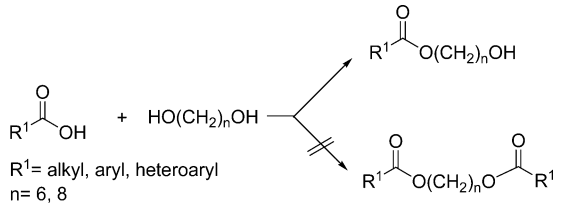
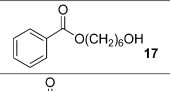
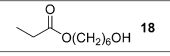
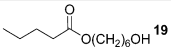
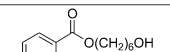
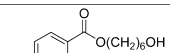
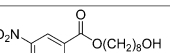
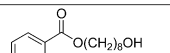
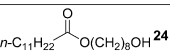
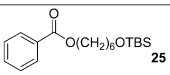
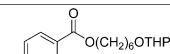
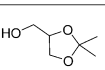
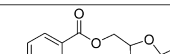



**Table 3. Selective Esterification of Carboxylic Acid under Optimized Conditions[a]**

| Entry | Acid | Alcohol | Product | Time | Yield (%) |
|---|---|---|---|---|---|
| 1 | $PhCO_2H$ | $HO(CH_2)_6OH$ |  **17** | 20 | 88<br>45[b] |
| 2 | Propionic acid | |  **18** | 18 | 91<br>45[b] |
| 3 | Pentanoic acid | |  **19** | 18 | 87 |
| 4 | 4-Methylbenzoic acid | |  **20** | 22 | 84 |
| 5 | 4-Nitrobenzoic acid | |  **21** | 20 | 92 |
| 6 | 3-Nitrobenzoic acid | $HO(CH_2)_8OH$ |  **22** | 20 | 84 |
| 7 | $PhCO_2H$ | |  **23** | 20 | 85 |
| 8 | Lauric acid | |  **24** | 18 | 91 |
| 9 | $PhCO_2H$ | $HO(CH_2)_6OTBS$ |  **25** | 22 | 84 |
| 10 | 4-Nitrobenzoic acid | $HO(CH_2)_6OTHP$ |  **26** | 20 | 86 |
| 11 | 4-Nitrobenzoic acid |  |  **27** | 20 | 92 |

[a]Reaction condition: carboxylic acid (1 mmol, 1 equiv), alcohol (1 equiv), 4-DMAP (3 equiv), **1** (1.5 equiv), 20 mL of THF-DCM (1:3 v/v mixture), room temperature. [b]Soluble triphenylphosphonium-iodide complex was used instead of reagent **1**.

The selective esterification of symmetrical diols is useful in many situations,[21] and has recently been addressed by Sharghi et al.[22] using $Al_2O_3$/ $MeSO_3H$ (AMA). The requirements of high acidic reaction environment, long reaction time and high temperature make this protocol unappealing. Although selective monoacylation of diol by enzymatic kinetic resolution is well-known,[23] the selectivity is due to configurational restriction for the formation of enzyme−substrate complex that leads to the acylated product. There is hardly any example of site selective enzymatic esterification of diols having no asymmetric center.[24] While solid-phase chemistry is well-suited to such problems,[25] we are unaware of any report in the literature of a selective monoesterification reaction in which the reacting species are not covalently attached to the polymer support. Gratifyingly,



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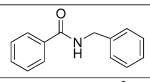
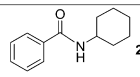
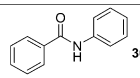
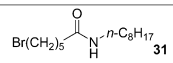
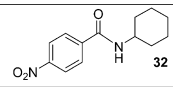
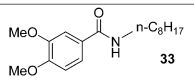
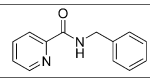
**Table 4. Amidation between Carboxylic Acid and Amine under Optimized Conditions**[a]

| Entry | Acid | Amine | Product | Time | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $PhCO_2H$ | $PhCH_2NH_2$ |  28 | 20 | 91 |
| 2 | |  |  29 | 20 | 92 |
| 3 | | $PhNH_2$ |  30 | 25 | 75 |
| 4 | 6-Bromohexanoic acid | $n\text{-}C_8H_{17}NH_2$ |  31 | 20 | 85 |
| 5 | 4-Nitrobenzoic acid |  |  32 | 20 | 86 |
| 6 | 3,4-Dimethoxybenzoic acid | $n\text{-}C_8H_{17}NH_2$ |  33 | 30 | 67 |
| 7 | Picolinic acid | $PhCH_2NH_2$ |  34 | 20 | 81 |

[a]Reaction condition: carboxylic acid (1 mmol, 1 equiv), amine (1 equiv), 4-DMAP (3 equiv), **1** (1.5 equiv), 20 mL THF-DCM (1:3 v/v mixture), room temperature. [b]Isolated yield.

the application of reagent **1** and DMAP to the esterification of benzoic acid with 1,6-hexanediol gave the desired monoester in 88% yield (Scheme 2). Inspired by this finding, we expanded this site-selective process to a variety of substrates as shown in Table 3. To our pleasure, the results obtained in the esterification of diols were, in general, good to excellent (entries 1−8). Various protecting groups like -OTBS (entry 9), -OTHP (entry 10) and acetals (entry 11) were unaffected under our reaction conditions. However, under our optimized condition, when soluble triphenylphosphonium-iodide was used instead of reagent **1**, monoesters were obtained in comparatively lower yields (entries 1−2).

The esterification reaction conditions proved to be useful for the synthesis of amides as well, as shown in Table 4. Primary aliphatic, secondary aliphatic, and aromatic amines all were incorporated with good yields.

Resin-bound triphenylphosphine, activated with iodine, has been shown here to be a convenient reagent for the preparation of esters and amides in the presence of DMAP as base. The requirement for 1.5 equiv of phosphine is counterbalanced by the recyclability of the resin-bound reagent, isolation of products by simple filtration, good yields, and by the utility of the reaction in generating monoesters from symmetrical diols.

## EXPERIMENTAL PROCEDURES

**General Procedure for the Synthesis of Ester and Amide.** To a stirred solution of preformed complex **1** (1.5 mmol) in 20 mL of anhydrous THF−DCM (1:3 v/v) was added 4-DMAP (3 mmol) and carboxylic acid (1 mmol) at ambient temperature. After the mixture was stirred for 10 min, alcohol or amine (1 mmol) was then added to the reaction mixture, and reaction mixture was allowed to stir for the time specified in the table. After completion of the reaction (as indicated by TLC), the resultant mixture was filtered and washes with dichloromethane (50 mL). The filtrate was then extracted and the combined organic layer was dried with anhydrous sodium sulfate and concentrated to give desired product in high purity.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscombsci.5b00086.

General experimental details, analytical data, and copies of $^1$H and $^{13}$C NMR spectra of compounds **7**, **10**−**12**, **17**, **18**, **21**, **28**−**30**, and **32** (PDF)

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### Notes

The authors declare no competing financial interest.

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