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COMMUNICATION

Significance of reagent addition sequence in the amidation of carboxylic acids mediated by PPh_3 and I_2

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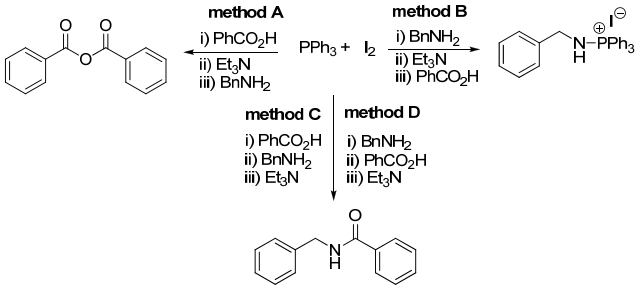
The outcome of the amidation reaction mediated by PPh_3-I_2 was found to be highly dependent on the addition sequence of the reagents. When triethylamine was subjected to a mixture containing PPh_3, I_2, and a carboxylic acid, acid anhydride was generated almost instantly before treatment with an amine presumably *via* an attack of carboxylate ion onto the acyl function of an acyloxyphosphonium salt. Nevertheless, when a PPh_3-I_2 mixture was treated with an amine, then a carboxylic acid, prior to adding the base, amide was rapidly formed in high yield with high chemoselectivity, most likely through an intermediacy of *O,N*-pentacoordinate phosphorane species as confirmed by ESI-MS technique.

Organic reactions mediated by phosphines play important roles in a number of functional group transformations including the classic Appel, Garegg-Samuelsson, Wittig, Mitsunobu, and Staudinger reactions.[1] Mechanistically, these reactions are driven by the strong oxophilicity of tertiary phosphines which, as a result, activate alcohols, carbonyl compounds, carboxylic acids and their derivatives toward nucleophilic substitution.

Among the available phosphines, triphenylphosphine (PPh_3) is highly attractive since it is inexpensive, readily available, and easy to handle.[1b, 2] Especially, in the preparation of carboxylic acid derivatives such as acid chlorides, amides, esters and thioesters, PPh_3 and its polymer bound analogs have been used in combination with various additives such as NCS,[3] NBS,[4] I_2,[5] I_2/Zn(OTf)$_2$ (Tf = trifluoromethylsulfonyl),[6] hypervalent iodine (III) reagent,[7] $BrCCl_3$,[8] and diethyl azodicarboxylate (Mitsunobu reaction)[9] for an *in situ* activation of a carboxylic acid prior to acyl displacement with an appropriate nucleophile.

A highly reactive acyloxyphosphonium species has been proposed as the key intermediate in these reactions which acted as an acylating agent for the acyl transfer process. Nevertheless, competitive formation of acid anhydride has often been encountered in several cases. Although its presence has been well documented,[5a, 5b, 9d] to the best of our knowledge, no further attempt has been made to circumvent this undesired side reaction. Recently, during the synthesis of *N*-acylbenzotriazoles from carboxylic acids mediated by PPh_3-I_2,[10] we also observed formation of benzoic anhydride upon mixing benzoic acid with PPh_3 and I_2 in the presence of triethylamine base. After a thorough investigation, we have discovered that when adding tertiary amine base in the last step, not only anhydride formation could be prevented, but the desired products also rapidly formed in high yields. This observation prompts us to extend our investigation toward amide bond formation using various amines with a range of nucleophilicity. Although the amidation mediated by PPh_3-I_2 has previously been reported,[5b] the reaction gave relatively low yields of the amides and, in some cases, required long reaction times with large excess of reagents possibly due to an involvement of anhydride side reaction. Thus, in this study, the utility of PPh_3-I_2 combination was re-explored. Indeed, the outcome of reaction was found to be highly dependent on sequences of reagent addition. Herein, we wish to report a new improved protocol for amidation of carboxylic acids mediated by PPh_3-I_2 which allows rapid access to a series of amides in good to excellent yields with high chemoselectivity.

In our preliminary studies, the amidation mediated by PPh_3-I_2 was investigated in the reaction between benzoic acid and benzyl amine as model substrates. The outcome of the reactions using different sequences of reagent addition was carefully examined within 10 min after the last reagent was added.



Scheme 1 Outcomes of the reactions between benzylamine and benzoic acid following different sequences of reagents addition.

As shown in Scheme 1 (method A), when benzoic acid was added to the mixture containing PPh_3-I_2 in the presence of Et_3N, benzoic anhydride was exclusively obtained almost instantly within 5 min. After 10 min stirring in the presence of benzylamine, no detectable amount of the amide product was observed possibly due to the relatively low reactivity of the formed anhydride. When benzylamine was added to the PPh_3-I_2 mixture, followed by addition of Et_3N then benzoic acid (method

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B), no trace of the corresponding amide could be detected either. Nevertheless, we were able to isolate a major component from this reaction which was identified as (benzylamino)triphenylphosphonium iodide[11] based on spectroscopic analysis. To our delight, it was found that when the amine base was added in the last step (methods C and D), *N*-benzylbenzamide was obtained quantitatively within 10 min.

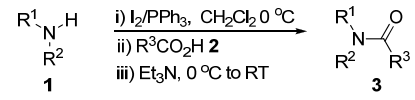
Since method C required longer time than method D for acid activation (see supplementary information for details), the scope and limitation of the developed protocol were further evaluated following the procedure described for method D except that the reaction time was varied depending on the reactivity of the substrates. Different types of aliphatic and aromatic amines were treated with various carboxylic acids including aromatic acids, aliphatic acid, and heterocyclic acid. According to Table 1, treatment of amines **1** with carboxylic acids **2** generally provided amides **3** in good to excellent yields within short reaction times. Quantitative yields of amides were obtained in the reactions between primary amines and benzoic acid (entries 1-2). The reaction with sterically hindered *tert*-butylamine also gave high product yield (entry 3). Secondary aliphatic amines as well as primary aromatic amines gave the corresponding amides in good yields (entries 4-7). However, the reaction with electron deficient 4-nitroaniline was sluggish providing the product in low yield (entry 8). No significant difference based on the electronic effect of the substituents on benzoic acid was observed in the reactions with cyclohexylamine (entries 9-11) although the presence of strong withdrawing nitro group on benzoic acid resulted in a slightly lower yield (entry 11).

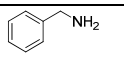
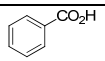
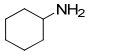
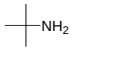
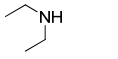
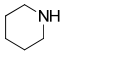
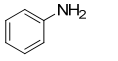
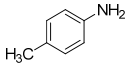
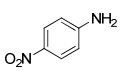
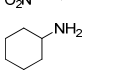
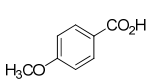
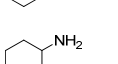
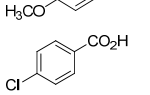
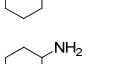
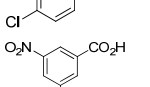
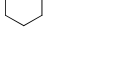
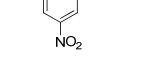
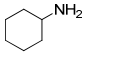
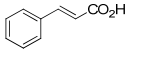
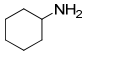
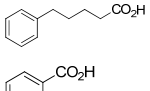
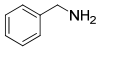
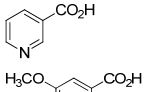
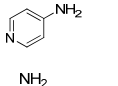
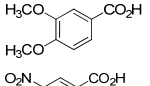
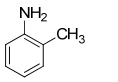
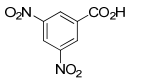
Cinnamic acid exclusively gave 1,2 addition product without Michael addition product or double bond isomerization (entry 12). In case of aliphatic acid, 5-phenylvaleric acid provided the expected amide in moderate yield under relatively long reaction time (entry 13). Lower yield from aliphatic acid in comparison to those with aromatic acids implied an involvement of π-π stacking interactions between aromatic acids and the phosphonium intermediates. For heterocyclic containing substrates, both nicotinic acid and 4-aminopyridine were viable reactants which underwent amidation without any interference (entries 14-15). In addition, the reaction between steric 2-methylaniline with 3,5-dinitrobenzoic acid and diethylamine with 2-napthanoic acid provided the corresponding amides in high yields (entries 16-17). It is interesting to note that, with our developed strategy, both the reaction times and the product yields were significantly improved in comparison to those derived from the previously reported method using the PPh_3/I_2 system[5b] as shown in parenthesis.

Another important factor to be considered when developing a new method in organic synthesis is chemoselectivity. We thus turn our attention to investigate functional groups compatibility of the protocol using carboxylic acids containing reactive functionalities such as hydroxyl and amino groups as well as *N*-protected α-amino acids with *tert*-butyloxycarbonyl (Boc), benzyloxycarbonyl (Cbz), and 9-fluorenylmethyloxycarbonyl (Fmoc) groups. The standard reaction condition was applied with all substrates without further optimization. As shown in Figure 1, primary aliphatic or aromatic amines reacted smoothly with 4-hydroxybenzoic acid or 4-hydroxy-3-methoxybenzoic acid to provide **3a**-**3d** in good yields. Combination between the heterocyclic 2-picolylamine with nicotinic acid also afforded amide **3e** in moderate yield. In the cases of benzoic acid derivatives pending with amino group, due to their limit solubility in dichloromethane, the amide products **3f** and **3g** were obtained in moderate yields. Interestingly, no side products from acylation of the arylamino groups were detected indicating the reactions were highly chemoselective.

Benzylamine reacted with *N*-Boc-protected glycine to afford the amide **3h** in quantitative yield. However, with the highly steric hindered *N*-Cbz-protected phenylalanine, low yield

Table 1 Synthesis of amides promoted by Ph_3P-I_2 system[a,b]



entry	NHR^1R^2 **1**	R^3CO_2H **2**	time (min)	% yield of **3**[Ref]
1			10(90)	99(77)[5b]
2			10	99[12]
3			30(720)	93(80)
4			30(60)	89(63)[5b]
5			30	82[13]
6			30	86[14]
7			15(360)	90(53)[5b]
8			60	27
9			15	95[15]
10			15	96[16]
11			30	88[17]
12			15	87
13			60	75[18]
14			60	98[19]
15			60	87[20]
16			60(180)	94(52)[5b]
17			60(720)	99(60)[5b]

[a]The reactions were carried out by adding amine (0.49 mmol) into a mixture containing I_2 (0.49 mmol) and PPh_3 (0.49 mmol) at 0 °C under N_2. After stirring at 0 °C until amine was no longer observed by TLC (~5-30 min), carboxylic acid (0.41 mmol) was added, followed by adding Et_3N (0.82 mmol). The mixture was further stirred at room temperature for a specified time. [b]The reaction times and the product yields of the reported method using PPh_3-I_2 as the acid activator[5b] were given in parenthesis.

Benzylamine reacted with *N*-Boc-protected glycine to afford the amide **3h** in quantitative yield. However, with the highly steric hindered *N*-Cbz-protected phenylalanine, low yield

of the amide **3i** was obtained. In the reaction with Fmoc-protected glycine, partially cleavage of the Fmoc group was observed by TLC indicating that the applied reaction condition was incompatible with the Fmoc group.

Since there are several reports using polymer supported PPh_3 (PS-PPh_3) to facilitate product purification,[5b, 5c, 9e] our reaction condition was further examined using PS-PPh_3 instead of the free phosphine in the synthesis of the amides **3a-i**. As shown in Figure 1, it was found that, in most cases, the respective amides could be prepared in comparative yields using 1.5 equiv each of PS-PPh_3 and I_2.

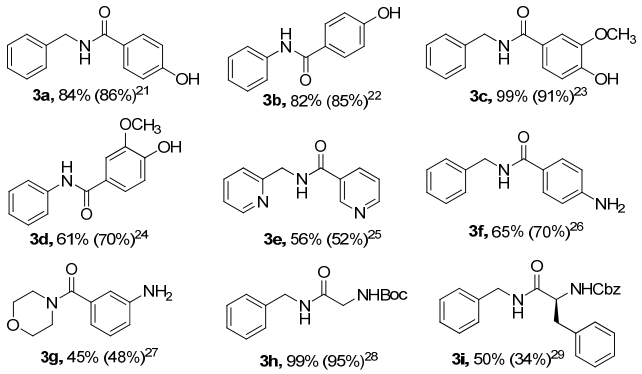


Figure 1 Synthesis of amides from carboxylic acids containing various functionalities using PPh_3 and PS-PPh_3 (the yields obtained with PS-PPh_3 were given in parenthesis).

To explain why the sequence of reagent addition is so crucial, $^{31}P\{H\}$ NMR studies of the reaction between benzylamine and benzoic acid were carried out in an NMR tube following the sequence of reagent addition in the methods A-D using $CDCl_3$ as a solvent. ^{31}P NMR spectra were recorded after each addition. Based on the results obtained (see Figure S1-S4 in supporting information for details), the general mechanisms for these reactions were proposed as shown in Scheme 2. The ^{31}P chemical shifts of the plausible intermediates were listed accordingly.

In all reactions, addition of I_2 to a solution of PPh_3 resulted in a slight shift of the free phosphine signal with an appearance of two new resonance peaks at around 45 and -17 ppm which were assigned to a slow equilibrium between triphenylphosphonium iodide (**I_a**) and pentacoordinate phosphorus diiodide (**I_b**), respectively.[5a-c] Under method A, addition of benzoic acid to **I** caused a slight shift of the signal at -16.93 to -14.83 ppm which could be contributed to the formation of an intermediate **II**. In the presence of Et_3N, acid anhydride formed spontaneously with concomitant released of Ph_3PO (29.50 ppm).[5c] This data suggested the intermediacy of an acyloxyphosphonium ion **III** though this species could not be observed directly due to its high reactivity. After addition of benzylamine, amide bond formation did not proceed within the 10 min observation time.

In method B, treatment of the intermediates **I** with benzylamine led to a rapid formation of solid precipitate. $^{31}P\{H\}$ NMR spectrum of the solution showed an appearance of a ^{31}P signal at 39.20 ppm (major) as well as two minor peaks at -18.70 and 35.50 ppm (broad) which could be attributed to the presence of aminophosphonium iodide,[11] and possibly a pentavalent phosphorus species **IV** as well as an iminiumphosphorane **V**, respectively.[5a, 30] Upon addition of Et_3N, the solids which could be ammonium salts including **IV** and **V** became dissolve. As a result, the equilibrium was shifted toward the formation of aminophosphonium iodide. This species was inactive toward the applied acid and thus gave no amide product under the subjected reaction condition.

In method C, addition of benzoic acid to **I** led to a slight shift of the ^{31}P signals. The shift of the peak at -16.82 to-13.85 ppm could be due to the formation of specie **II**. Subsequent treatment with benzylamine resulted in solid precipitate, while the ^{31}P NMR spectrum revealed three new resonance peaks at δ_p 39.21 ppm (minor), 34.55 (minor, broad) and -16.27 ppm (major). At this stage, acid-base reaction between the acid and amine is most likely to be predominant which shifted the equilibrium toward species **Ia** (-16.27 ppm). Aminophosphonium iodide (39.21 ppm) and the intermediate **IV** could be generated from the remained amine as minor components. Upon treatment with Et_3N, all the formed solids became soluble. A release of Ph_3PO (29.48 ppm) with concomitant formation of the amide product (based on TLC) indicated that the reaction might proceed through an acyloxyphosphonium ion **III** or possibly via an *O,N*-pentacoordinate phosphorane **VI**.[4b,9f] The presence of an amine when **III** is being generated seems to be crucial in preventing the anhydride formation.

In method D where the addition of the carboxylic acid and the amine was reversed, treatment of **I** with benzylamine again resulted in solid precipitate. ^{31}P-NMR spectrum of the mixture revealed the presence of aminophosphonium iodide (39.16 ppm, major) as well as the ammoniumphosphorane **IV** (-18.74 ppm, minor) and iminiumphosphorane **V** (35.56 ppm, minor). Addition of a carboxylic acid did not lead to any significant change in these ^{31}P signals. However, in the presence of Et_3N where all the solids dissolved, apart from the remained aminophosphonium iodide (38.90 ppm), Ph_3PO (29.50 ppm) was generated spontaneously upon amide bond forming.

When the ESI-MS technique was used to monitor the reaction at the early stage of Et_3N addition, the mass spectrum revealed a major peak at m/z 368.1576 which was assigned to the imminiumphosphorane **V** and (benzylamino)triphenylphosphonium salt (see Figure S5 in supporting information). Interestingly, we were able to observe a peak at m/z 490.1915 which confirmed the presence of the proposed pentacoordinated phosphorous intermediate **VI**. This data strongly suggested that this reaction proceeded mainly via an attack of benzoate anion on to the phosphorus center of **V**. The generated species **VI** then concomitantly activates both the carboxylic acid and the amine moieties to participate in an intramolecular acyl transfer process to provide an amide with a release of Ph_3PO. It is important to point out that although the commonly proposed acyloxyphosphonium intermediate **III** could not be detected by both ^{31}P NMR and ESI-MS techniques, its formation still could not be completely ruled out since the reaction was under equilibrium.

In summary, a new improved protocol for amidation of carboxylic acids mediated by PPh_3-I_2 system was described through changing the sequence of the reagents addition. The method is proven to be mild, highly effective with functional group tolerant and high chemoselectivity. Since acyloxyphosphonium species have been proposed to involve in various nucleophilic acyl substitution reactions which should not only be limited to the PPh_3-I_2 activation, this technique could be potentially applied with other phosphine mediated systems which will greatly enhance the reactions in terms of the reaction rate, product yields, and selectivity.

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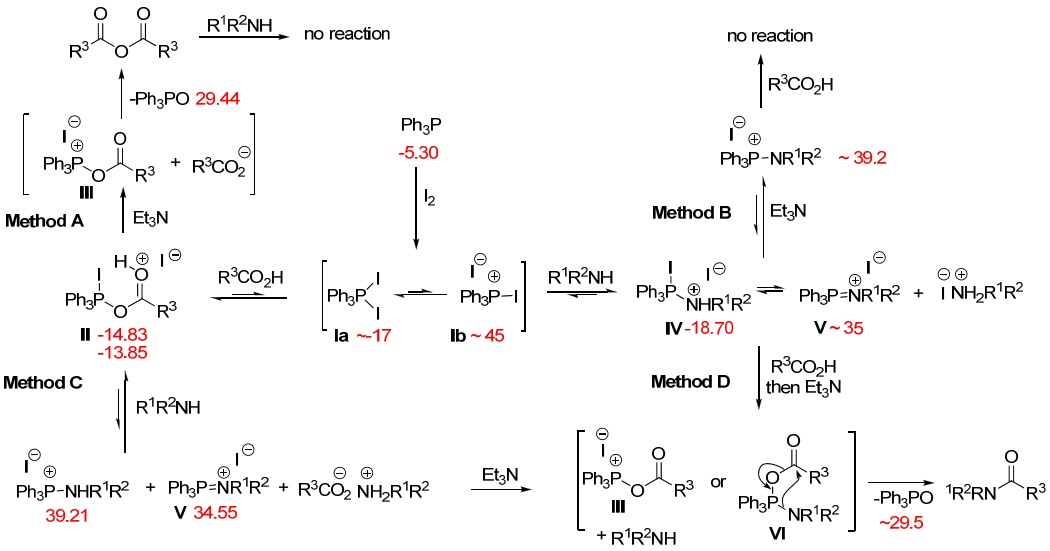

Scheme 2. Proposed mechanism for the reactions mediated by Ph_3P-I_2 system following the methods A, B, C, and D. ^{31}P NMR chemical shifts of important intermediates were given for R^1 = Ph, R^2 =H, and R^3 = Ph.

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