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PPh_3/Selectfluor-Mediated Transformation of Carboxylic Acids into Acid Anhydrides and Acyl Fluorides and its application in amide and ester synthesis

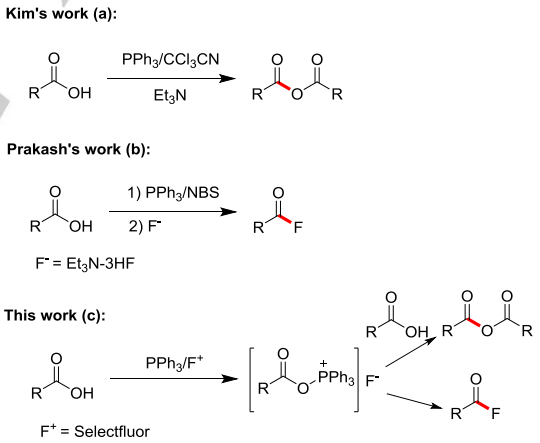
Zhen Yang,[a] Siwei Chen,[a] Fang Yang,[a] Chenxi Zhang,[a] You Dou,[a] Qiuju Zhou,[a] Yizhe Yan,[b] and Lin Tang*[a]

Abstract: By taking the advantage of PPh_3/Selectfluor system, carboxylic acids are efficiently converted into the pivotal intermediates of acyloxyphosphonium ions that can selectively react with a second carboxylic acid or fluoride to in situ yield the corresponding acid anhydrides or acyl fluorides. The developed protocol features commercial availability of reagents, no involvement of base, room temperature conditions and simple experimental procedure. Additionally, various amides or esters are readily achieved, respectively, with the addition of amines or alcohols.

Introduction

Carboxylic acid derivatives, including acid anhydrides and acyl fluorides, are important and versatile intermediates in synthetic, medicinal and material chemistry since these structural motifs afford straightforward access to a variety of high-value amides, esters and other functional compounds.[1] In this context, the significant number of strategies have been successfully achieved for the preparation of the above carboxylic acid derivatives. For example, acid anhydrides are usually prepared through reactions of carboxylic acids with dehydrative partners, such as phosgene,[2] thionyl chloride,[3] isocyanates,[4] 1,3,5-triazines,[5] Vilsmeier-Haack reagent,[6] carbodiimides,[7] phosphoranes[8] and pyridazin-3(*2H*)-ones,[9] and carboxylate salts with acylating reagents.[10] The reported protocols for acyl fluoride synthesis directly from carboxylic acids mainly rely on the use of cyanuric fluoride,[11] HF/pyridine/DCC complex,[12] SeF_4/pyridine,[13] sulfur-based fluorinating reagents[14] and $(Me_4N)SCF_3$.[15] However, the existing protocols remain limited because of non-commercial availability of starting materials, toxicity, thermal instability, high reaction temperature and low functional group compatibility. Therefore, exploring a more practical and convenient approach to synthesis of acid anhydrides and acyl fluorides is highly desirable.

Organophosphorus compounds, which serve as efficient coupling reagents to activate alcohols, have been extensively applied in Mitsunobu[16] and Appel[17] reactions. In addition, carboxylic acids could also be activated by phosphorus reagents to afford the amides or esters.[18] Recently, PPh_3/CCl_3CN-promoted transformation of carboxylic acids was developed by Kim and Jang as a supplemental method for acid anhydride synthesis, even though toxic CCl_3CN and additional triethylamine were used.[19] Very recently, Prakash and co-workers successfully disclosed a protocol for the synthesis of acyl fluorides from carboxylic acids by use of a PPh_3/NBS/Et_3N-3HF system.[20] However, additional NBS and dangerous Et_3N-3HF were required. Encouraged by these achievements and our interest in green synthesis,[21] especially in organofluorine chemistry,[22] we envisioned that PPh_3 and Selectfluor might activate carboxylic acids to offer acyloxyphosphonium ions and F^- (F^- was generated from F^+ in situ). Then, a second carboxylic acid or F^- could attack the acyloxyphosphonium ions, affording the corresponding acid anhydrides or acyl fluorides (Scheme 1c). The proposed protocol employed commercially available reagents PPh_3 and Selectfluor at room temperature without the involvement of base. Upon adding amines or alcohols, the construction of amides or esters was efficiently realized.



Scheme 1. Phosphorus reagents-mediated transformation of carboxylic acids into acid anhydrides and Acyl Fluorides.

Results and Discussion

As depicted in Table 1, 4-methylbenzoic acid (**1b**) was chosen as the model substrate to optimize the reaction conditions. The effect of alkaline additves was initially investigated in the presence of PPh_3/Selectfluor. The corresponding product **2b** was obtained in 78% and 84% yields, when K_2CO_3 and Et_3N were added to the reaction, respectively (entries 1 and 2). Interestingly, an excellent yield of 92% was achieved without any additive (entry 3). Subsequent experiments were carried out to evaluate various solvents (entries 4-7). CH_3CN could afford **2b** in 93% yield, and relative low yields were obtained in THF

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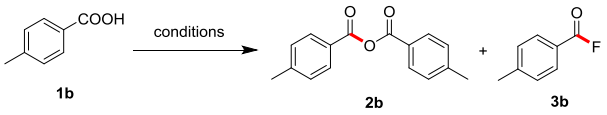
and DMF. However, the construction of **2b** was absolutely suppressed when DMSO was employed as the solvent, which is probably due to the side reaction of DMSO with Selectfluor. As contrast, other organophosphorus compounds, such as $P(OEt)_3$ and $P(n\text{-}Bu)_3$, were also evaluated, and no higher yield was achieved (entries 8 and 9). Further study indicates that reducing the amount of coupling reagents is unfavourable to the reaction (entry 10). In addition, the yield of **2b** was slightly decreased when the reaction temperature was increased to 50 °C. The above results show that the formation of **3b** is difficult.

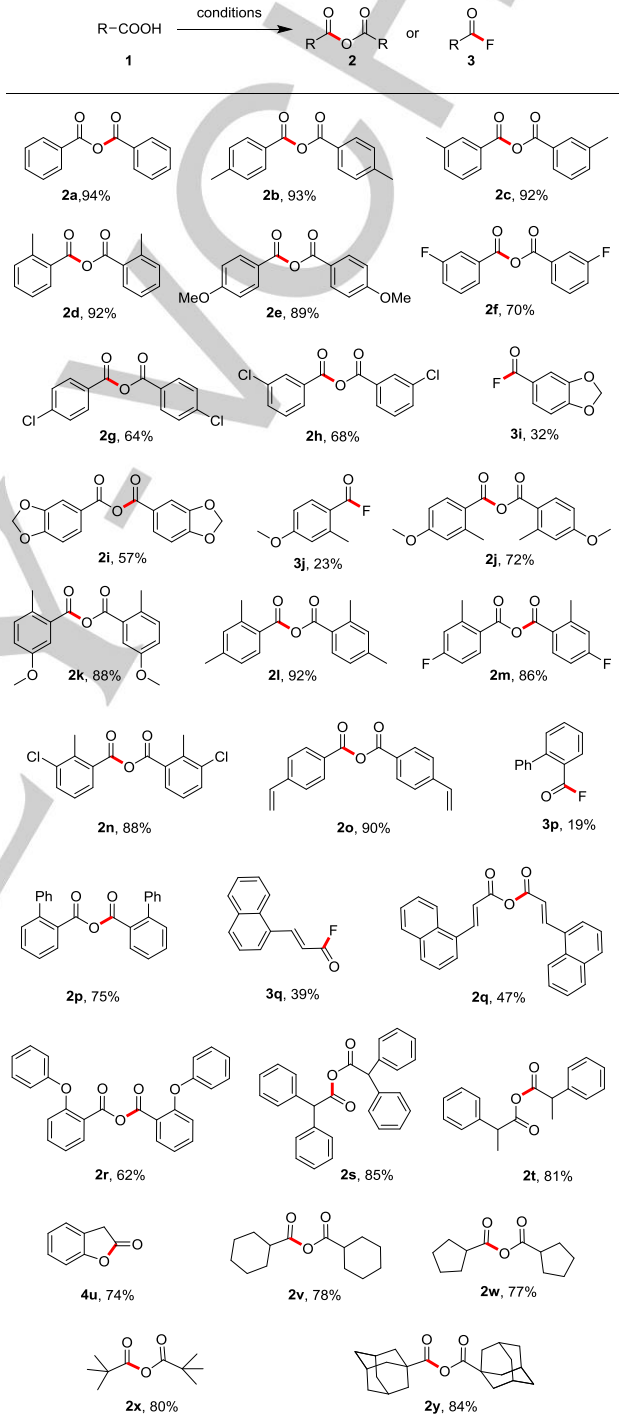
Table 1. Optimization of reaction conditions.[a]



Entry	Coupling reagent	Additive	Solvent	Yield [%][b]	
				2b	**3b**
1	PPh_3/Selectfluor	K_2CO_3	CH_2Cl_2	78	< 5
2	PPh_3/Selectfluor	Et_3N	CH_2Cl_2	84	trace
3	PPh_3/Selectfluor	--	CH_2Cl_2	92	n.d.
4	***PPh_3/Selectfluor***	**--**	***CH_3CN***	***93***	***trace***
5	PPh_3/Selectfluor	--	THF	78	trace
6	PPh_3/Selectfluor	--	DMSO	n.d.	trace
7	PPh_3/Selectfluor	--	DMF	82	trace
8	$P(OEt)_3$/Selectfluor	--	CH_3CN	59	n.d.
9	$P(n\text{-}Bu)_3$/Selectfluor	--	CH_3CN	88	trace
10[c]	PPh_3/Selectfluor	--	CH_3CN	77	trace
11[d]	PPh_3/Selectfluor	--	CH_3CN	91	trace

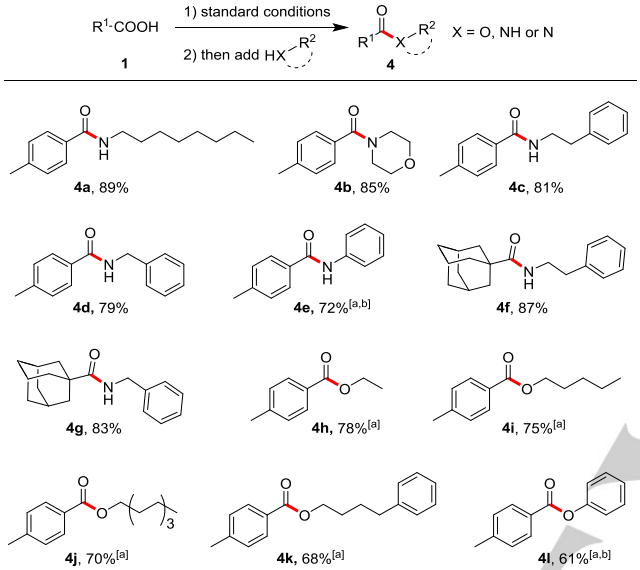
[a] Reactions conditions: **1b** (0.25 mmol), organophosphorus compound (0.30 mmol), Selectfluor (0.30 mmol), additive (0.3 mmol), solvent (1.0 mL), room temperature, 4 h, N_2 atmosphere. [b] Isolated yield; n.d. = not detected. [c] PPh_3 (0.25 mmol), Selectfluor (0.25 mmol). [d] 50 °C.

After confirming the optimized conditions, we attempted to extend the scope of carboxylic acids (Scheme 2). Excellent yields (> 89%) were obtained when electron-donating groups methyl and methoxyl appeared on the benzene ring (**2b-2e**). Carboxylic acids bearing weakly electron-withdrawing groups, such as fluoro and chloro, could afford the corresponding products **2f-2h** in good yields. Interestingly, the desired products of acyl fluorides **3i** and **3j** were isolated. Moreover, polysubstituted carboxylic acids could also afford the products **2k-2n** in 86-92% yields, regardless of the large steric hindrance. Products **2o**, **2p** and **2r** bearing 4-vinyl, 2-phenyl and 2-phenoxyl, respectively, were readily achieved in moderate to good yields. However, alkenyl acid **1q** represented low chemoselectivity, and the corresponding **3q** was obtained up to 39% yield. A lactone **4u** were given via intramolecular dehydration when 2-(2-hydroxyphenyl)acetic acid was used as the substrate. In addition, reactions of various aliphatic acids, including phenylacetic, cyclohexanic, cyclopentanic, *t*-butanic and adamantanic acid, could take place smoothly to give the target materials **2s-2y** in good yields. It is interesting to note that acyl fluorides were observed after all the reactions by ^{19}F NMR analyses, although most of them could not be isolated.

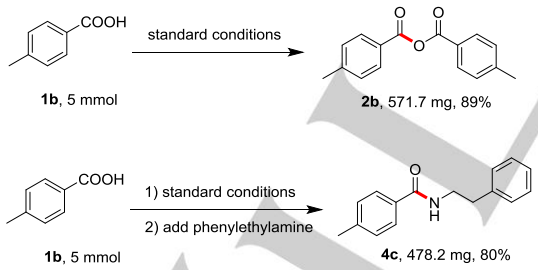


Scheme 2. Reaction conditions: **1** (0.25 mmol), PPh_3 (0.30 mmol), Selectfluor (0.30 mmol), CH_3CN (1.0 mL), room temperature, 4 h, N_2 atmosphere; isolated yield.

A tandem amidation or esterification was readily achieved with the addition of amines or alcohols to the reaction mixture (Scheme 3). Aliphatic amines such as *n*-octylamine, morpholine, phenylethylamine and benzylamine were successfully employed as the substrates, affording the corresponding products (**4a-4d**, **4f** and **4g**) in good yields. Increasing the reaction temperature could also offer the desired esters **4h-4k** using alcohols as the substrates. In addition, aniline and phenol were also active substrates with the assistance of K_2CO_3. Compared to previous reports, this protocol avoids the isolation of acid anhydrides and acyl fluorides.[23,24]



Scheme 3. Reaction conditions: 1) **1** (0.25 mmol), PPh_3 (0.30 mmol), Selectfluor (0.30 mmol), CH_3CN (1.0 mL), room temperature, 4 h, N_2 atmosphere; 2) then amines or alcohols (0.125 mmol), room temperature, 4 h, N_2 atmosphere, isolated yield. [a] 80 °C. [b] K_2CO_3 (0.125mmol).

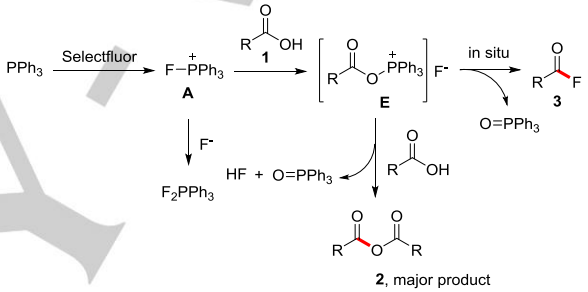


Scheme 4. Scale-up experiments under standard conditions.

The scale-up reactions were carried out under standard conditions to further assess the synthetic utility of the developed protocol. Pleasingly, 5 Mmol of **1b** could give the desired products **2b** and **4c** in good yields (Scheme 4).

To gain insight into the possible mechanism of these transformations, the corresponding control experiments were conducted (see the supporting information for details). Mixing PPh_3 with Selectfluor led to the construction of fluorophosphonium ion **A** with ^{31}P NMR signal at δ 95.0 (d, J_{PF} = 994.4 Hz) and ^{19}F NMR signal at δ -128.7 (d, J_{PF} = 992.5 Hz). When **1b** was added to the above reaction mixture, the ^{31}P and ^{19}F NMR signals of fluorophosphonium ion **A** rapidly disappeared. And a new peak with ^{31}P NMR signal at δ 64.7 (s) was observed, which were assigned to the pivotal species acyloxyphosphonium ion **E**. Another new ^{19}F NMR signal of acyl fluoride **3b** at δ 15.9 (s) was represented. In addition, triphenylphosphine oxide and F_2PPh_3 were generated during the process with ^{31}P NMR signals at δ 30.2 (s) and 54.1 (t, J_{PF} = 655.1 Hz), respectively.

On the basis of the results above and previous reports,[20] a plausible reaction mechanism is proposed as shown in Scheme 5. The reaction of PPh_3 with Selectfluor generates fluorophosphonium ion **A**, which is rapid converted into acyloxyphosphonium ion **E** in the presence of carboxylic acid **1**. Another **1** then attacks **E** to give the major product acid anhydride **2** along with the generation of HF and triphenylphosphine oxide. The in-situ formed F^- from Selectfluor can also attack **E** to afford small amount acyl fluoride **3**.



Scheme 5. Proposed reaction mechanism.

Conclusions

In conclusion, PPh_3 and Selectfluor can serve as an efficient and simple reagent system to activate carboxylic acids, affording the desired acid anhydrides in good to excellent yields, as well as acyl fluorides in some cases. Mechanistic studies indicate that the reaction proceeds through active species of acyloxyphosphonium ions, which can be quickly converted into the final products in situ by a second carboxylic acid or F^-. Thus, this method represents prominent advantages of stable commodity chemicals, broad substrate scope, no use of base, room temperature conditions, scale-up synthesis and operational simplicity. Upon adding amines or alcohols, the formation of a wide array of amides or esters is readily realized. Further exploration of PPh_3/Selectfluor system are currently underway in our laboratory.

Experimental Section

General information

Proton nuclear magnetic resonance (^1H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra, ^{19}F fluorine spectra (^{19}F NMR) and ^{31}P phosphorus spectra (^{31}P NMR) were recorded on a JNM-ECZ600R/S3 (^1H NMR 600 MHz, ^{13}C NMR 150 MHz, ^{19}F NMR 564 MHz

and ^{31}P NMR 243 MHz). HRMS were recorded on a MicroMass Waters Xevo G2-XS QTof. A uncorrected Beijing Tech Instrument Co., LTD X-4 melting point apparatus was used to determine melting points. Unless otherwise indicated, all reagents were purchased commercially without further purification.

General reaction procedures for the synthesis of 2 and 3

To an ovened-dried 10 mL schlenk tube was added carboxylic Acid **1** (0.25 mmol), PPh_3 (0.30 mmol) and Selectfluor (0.30 mmol). The tube was evacuated and back-filled with nitrogen, which was repeated three times. Anhydrous CH_3CN (1.0 mL) was then added to the reaction mixture via syring. The above mixture was stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography on silica gel with hexane and ethyl acetate (v:v = 30:1 to 5:1) as eluent to give the desired product **2** and **3**.

General reaction procedures for the synthesis of 4

To an ovened-dried 10 mL schlenk tube was added carboxylic Acid **1** (0.25 mmol), PPh_3 (0.30 mmol) and Selectfluor (0.30 mmol). The tube was evacuated and back-filled with nitrogen, which was repeated three times. Anhydrous CH_3CN (1.0 mL) was then added to the reaction mixture via syring. The above mixture was stirred at room temperature for 4 h. After the reaction was finished, amine or alcohol (0.125 mmol) was added. Then, the aforementioned mixture continued to be stirred at room temperature or 80 ^oC for 4 h. The resulting mixture was concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography on silica gel with hexane and ethyl acetate (v:v = 8:1 to 3:1) as eluent to give the desired product **4**.

Acknowledgements

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Keywords: triphenylphosphine • Selectfluor • carboxylic acids • acid anhydrides • acyl fluorides

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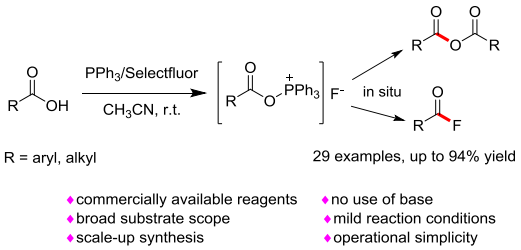
An efficient synthesis of acid anhydrides or acyl fluorides mediated by PPh_3/Selectfluor synstem is reported. Mechanistic studies show that the reaction proceeds through active species of acyloxyphosphonium ions, which can be quickly converted into the final products in situ by a second carboxylic acid or F^-.



Carboxylic Acid Derivatives

*Z. Yang, S. Chen, F. Yang, C. Zhang, Y. Dou, Q. Zhou, Y. Yan, and L. Tang**

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