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Synthesis of Functionalized Furans via Chemoselective Reduction/Wittig Reaction Using Catalytic Triethylamine and Phosphine

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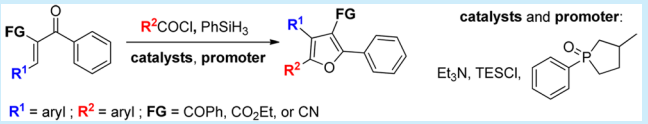
Supporting Information

ABSTRACT: An efficient protocol for the synthesis of highly functionalized furans via intramolecular Wittig reaction has been developed using catalytic amounts of phosphine and triethylamine. Silyl chloride served as the initial promoter to activate the phosphine oxide. Reduction of the activated phosphine oxide by hydrosilane resulted in generation of phosphine, while decomposition of Et_3N·HCl resulted in regeneration of base, which mediated formation of phosphorus ylide. Remarkably, the in situ generated byproduct, Et_3N·HCl, also catalyzes reduction of phosphine oxide.

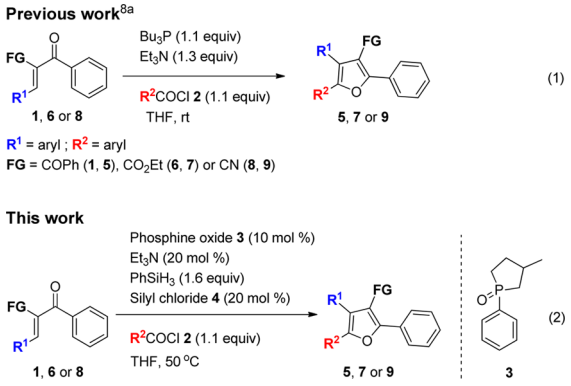


Phosphine-mediated transformations[1−4] are ubiquitous in synthetic chemistry and have a vast impact on this field. Although these applications are very useful, the in situ generated stoichiometric amount of phosphine oxide byproduct makes the purification process difficult and poses environmental hazards, rendering them less practical on an industrial scale. In recent years, protocols involving recyclable usage of phosphine reagents have attracted much attention.[5] Hydrosilane has potential for phosphine oxide reduction, which makes this concept possible.[6] Each of these earlier protocols has its own limitations, such as use of excess base or harsh reaction conditions which do not allow substrates that are sensitive toward such conditions to be employed. The challenges in this design are achieving chemoselective reduction of phosphine oxide without affecting the accompanying reagents or substrates[5] and forming byproducts, serving as the catalyst/cocatalyst in a multistep reaction to benefit the main reaction course[7] or are orthogonal.

We previously reported the synthesis of furans via intramolecular Wittig reaction by treating simple Michael acceptors with tributylphosphine, triethylamine, and acyl chlorides **2** under mild conditions (Scheme 1, eq 1).[8] Here, we report a novel protocol for the synthesis of these furans utilizing a catalytic amount of phosphine reagent (Scheme 1, eq 2). Notably, silyl chloride and the in situ generated byproduct, triethylammonium chloride, are found to accelerate the reduction of phosphine oxide.

We first selected the α-cyano-substituted chalcone **1a** and 4-chlorobenzoyl chloride (**2a**) as the substrates to test the feasibility of the catalytic Wittig reaction (Table 1). To promote the phosphine oxide reduction and in situ generate phosphorus ylide, more than 2 equiv of base was used (Table 1, entries 1−3). Although the reaction did not work well at 30 °C, mild heating to 50 °C improved the yield slightly (Table 1, entries 1 and 2). While excess **2a** was utilized, a higher yield of adduct **5aa** was obtained (Table 1, entry 3). Decreasing the amount of Et_3N could promote the reaction even better (Table 1, entry 4). It is

Scheme 1. Synthesis of Highly Functionalized Furans via Intramolecular Catalytic Wittig Reaction



possible that **2a** is reduced into the corresponding aldehyde and that Michael acceptor **1a** is reduced under these reaction conditions.[7d,9] We also assumed that the silyl alcohol formed in the reaction would trap the acyl chloride, and use of excess **2a** was required. Therefore, **4a** was chosen as the trapping reagent for in situ generated silyl alcohol and thereby reduced the need for excess **2a**. **4a** and **2a** (1.1 equiv, Table 1, entry 5) provided results similar to that in Table 1, entry 4. Even a catalytic amount of Et_3N could facilitate the reaction (Table 1, entry 6). Increasing the amount of phenylsilane improved the yield (Table 1, entry 7). We found that the reaction still performed well by decreasing the loading of **4a** to 50 mol % (Table 1, entry 8). We employed triethylsilyl chloride (**4b**) instead of volatile **4a** to further reduce the loading of silyl chloride (Table 1, entries 9 and 10). The best result was afforded using 20 mol % of **4b** and 1.6 equiv of phenylsilane (Table 1, entry 10). Good results with catalytic

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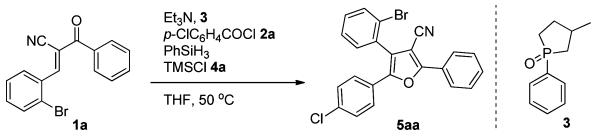
Table 1. Optimization of Reaction Conditions[a]



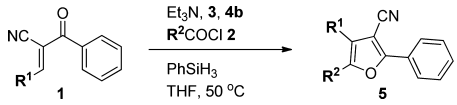
entry	Et_3N (equiv)	$PhSiH_3$ (equiv)	4a (equiv)	2a (equiv)	time (h)	5aa, yield (%)[b]
1[c]	2.7	1.0		1.1	24	14
2	2.7	1.0		1.1	14	26
3	2.7	1.0		2.2	14	68
4	1.1	1.0		2.2	8	68
5	1.1	1.0	1.1	1.1	13	65
6	0.2	1.0	1.1	1.1	12	52
7	0.2	1.4	1.1	1.1	12	67
8	0.2	1.4	0.5	1.1	12	58
9	0.2	1.4	0.2[d]	1.1	6	59
10	0.2	1.6	0.2[d]	1.1	5	84

[a]Reaction carried out using **1a** (0.3 mmol), Et_3N, **2a**, **3** (10 mol %), phenylsilane, and **4a** in dry THF (1.5 mL) under Ar atmosphere. [b]Isolated yield. [c]30 °C. [d]**4b** was used instead of **4a**.

amounts of **4b** indicate the role of silyl chloride as a promoter for the reduction of phosphine oxide instead of acting as a trapping reagent for the in situ generated silyl alcohol, as assumed earlier.[10]

With the optimized conditions, the protocol was first investigated using different α-cyano-substituted chalcones **1** and **2** to synthesize various furan adducts **5**. First, **1a** was examined with a variety of **2** (Table 2, entries 1−8). The effect of

Table 2. Synthesis of Furan Derivatives 5 from 1[a]



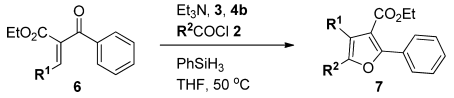
entry	R^1	R^2	time (h)	5, yield (%)[b]
1	**1a**, 2-BrPh	**2a**, 4-ClPh	5	**5aa**, 84
2	2-BrPh	**2b**, 3-ClPh	6	**5ab**, 73
3	2-BrPh	**2c**, 2-ClPh	6	**5ac**, 61
4	2-BrPh	**2d**, 4-OMePh	12	**5ad**, 70
5	2-BrPh	**2e**, 4-MePh	12	**5ae**, 77
6	2-BrPh	**2f**, Ph	12	**5af**, 80
7	2-BrPh	**2g**, Cy	20	**5ag**, 33
8	2-BrPh	**2h**, ^{n}Pr	14	**5ah**, 66
9	**1b**, 4-BrPh	4-ClPh	6	**5ba**, 85
10	**1c**, 2-ClPh	4-ClPh	6	**5ca**, 94
11	**1d**, 4-NO_2Ph	4-ClPh	4	**5da**, 98
12	**1e**, Ph	4-ClPh	12	**5ea**, 93
13	**1f**, 2-thienyl	4-ClPh	6	**5fa**, 89
14	**1g**, 4-OMePh	4-ClPh	18	**5ga**, 63

[a]Reaction was carried out using **1** (0.3 mmol), Et_3N (20 mol %), **2** (1.1 equiv), **3** (10 mol %), phenylsilane (1.6 equiv), and **4b** (20 mol %) in dry THF (1.5 mL) under Ar atmosphere. [b]Isolated yield.

steric hindrance could be clearly observed in with *para*-, *meta*-, and *ortho*-chlorobenzoyl chlorides in the decreasing yields (Table 2, entries 1−3). Absence of an electron-withdrawing group or presence of an electron-donating group reduced the reactivity of acyl chloride (Table 2, entries 4−6). An aliphatic functionality as R^2 could also be introduced successfully under the reaction conditions, providing **5ag** or **5ah** in 33 or 66% yield, respectively (Table 2, entries 7 and 8). The reaction also proceeded well with different R^1 substituents (Table 2, entries 9−13) except for **1g**, where **5ga** was obtained in moderate yield (Table 2, entry 14).

This protocol worked well with different substrates **6** bearing an ester functionality to afford furans **7** under the same conditions (Table 3). A variety of desired products **7** were

Table 3. Synthesis of Furan Derivatives 7 from 6[a]

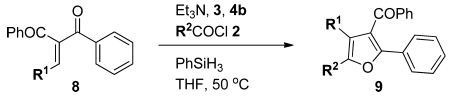


entry	R^1	R^2	time (h)	7, yield (%)[b]
1	**6a**, 4-NO_2Ph	**2a**, 4-ClPh	9	**7aa**, 85
2	4-NO_2Ph	**2b**, 3-ClPh	7	**7ab**, 92
3	4-NO_2Ph	**2c**, 2-ClPh	9	**7ac**, 88
4	4-NO_2Ph	**2d**, 4-OMePh	18	**7ad**, 62
5	4-NO_2Ph	**2e**, 4-MePh	15	**7ae**, 73
6	4-NO_2Ph	**2f**, Ph	12	**7af**, 82
7	4-NO_2Ph	**2i**, 4-NO_2Ph	9	**7ai**, 91
8	4-NO_2Ph	**2j**, 2-furyl	15	**7aj**, 76
9	**6b**, 4-CNPh	4-ClPh	10	**7ba**, 90

[a]Reaction was carried out using **6** (0.3 mmol), Et_3N (20 mol %), **2** (1.1 equiv), **3** (10 mol %), phenylsilane (1.6 equiv), and **4b** (20 mol %) in dry THF (1.5 mL) under Ar atmosphere. [b]Isolated yield.

obtained in moderate to good yields. Even Michael acceptors **8** with additional ketone functionality were successfully employed in this new protocol, furnishing furans **9** in high yields (Table 4).

Table 4. Synthesis of Furan Derivatives 9 from 8[a]



entry	R^1	R^2	time (h)	9, yield (%)[b]
1	**8a**, 4-NO_2Ph	**2a**, 4-ClPh	10	**9aa**, 92
2	4-NO_2Ph	**2b**, 3-ClPh	10	**9ab**, 97
3	4-NO_2Ph	**2c**, 2-ClPh	10	**9ac**, 94
4	4-NO_2Ph	**2d**, 4-OMePh	10	**9ad**, 92
5	4-NO_2Ph	**2f**, Ph	10	**9af**, 91
6	4-NO_2Ph	**2i**, 4-NO_2Ph	10	**9ai**, 89
7	4-NO_2Ph	**2j**, 2-furyl	7	**9aj**, 89
8	**8b**, 3-NO_2Ph	4-ClPh	36	**9ba**, 97
9	**8c**, 2-NO_2Ph	4-ClPh	10	**9ca**, 90
10	**8d**, 2-thienyl	4-ClPh	24	**9da**, 85
11	**8e**, CO_2Et	4-ClPh	7	**9ea**, 99

[a]Reaction was carried out using **6** (0.3 mmol), Et_3N (20 mol %), **2** (1.1 equiv), **3** (10 mol %), phenylsilane (1.6 equiv), and **4b** (20 mol %) in dry THF (1.5 mL) under Ar atmosphere. [b]Isolated yield.

When the reaction was carried out with **1h** and sterically congested **2k**, the chemoselective Wittig reaction took place as in our earlier studies[8b] to furnish **10** in 66% yield (Scheme 2).

To understand the exact role of each reagent in our protocol, we conducted a series of control experiments for the reduction of **3** (Table 5). During the optimization of our protocol (Table 1), it was evident that Et_3N and the in situ generated Et_3N·HCl could play an important role in the phosphine oxide reduction. Hence, we monitored the progress of phosphine oxide reduction using different ratios of Et_3N and Et_3N·HCl that would account for 2

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Scheme 2. Synthesis of the Functionalized Benzofuran 10

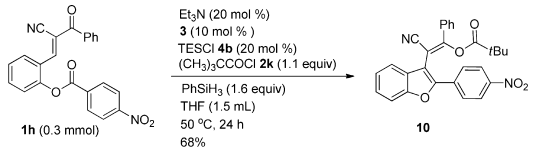
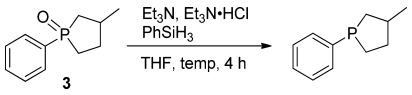


Table 5. Control Experiments for Reduction of Phosphine Oxide 3[a]



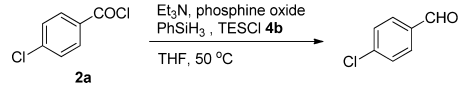
entry	Et_3N (equiv)	Et_3N·HCl (equiv)	temp (°C)	yield (%)[b]
1	2.0	0.0	30	33
2	0.0	2.0	30	0
3	0.2	1.8	30	0
4	1.8	0.2	30	42
5	0.0	2.0	50	73
6[c]	2.0	0.0	30	70
7[c]	2.0	0.0	50	82[d]
8[c,e]	2.0	0.0	50	0

[a]Reaction was carried out using **3** (0.2 mmol), phenylsilane (18 equiv), Et_3N, and Et_3N·HCl in dry THF (1.0 mL) under Ar atmosphere. [b]Determined by ^{31}P NMR analysis of the crude reaction mixture. [c]**4b** (2 equiv) was added. [d]2 h. [e]$P(O)Bu_3$ was used instead of **3**.

equiv compared to **3**. At 30 °C, a catalytic amount of Et_3N·HCl accelerated the rate of reduction (Table 5, entries 1 and 4). Reduction was very slow in the absence of Et_3N or with a catalytic amount of Et_3N, even when a stoichiometric amount of Et_3N·HCl was employed (Table 5, entries 2 and 3). Reduction of **3** was also efficient solely with Et_3N·HCl at 50 °C (Table 5, entry 5). This result indicates that, under the mild heating condition, a portion of HCl can escape from the system to regenerate Et_3N from Et_3N·HCl for the reduction of phosphine oxide.[11] Moreover, **4b** afforded a better result (Table 5, entries 1 and 6). Silyl chloride species could accelerate the reduction by activation of **3**.[10] A combined effect of **4b** and a higher temperature was observed in Table 5, entry 7, which gave the best result. We utilized the conditions in Table 5, entry 7, to carry out the reduction of tributylphosphine oxide (Table 5, entry 8). No reduction of phosphine oxide was observed in this case. This shows the advantage of using **3** rather than $P(O)Bu_3$ in our catalytic system.

To study the possible side reactions of acyl chloride in the reduction process (which used excess acyl chloride during the initial optimization of the catalytic Wittig reaction), we exposed **2a** to our reduction conditions (Table 6). No reduction of acyl chloride was observed in the absence of phosphine oxide (Table 6, entry 1). In the presence of **3**, considerable reduction of **2a** was observed at 30 °C (Table 6, entry 2). The efficiency of acyl chloride reduction increased at higher temperature (Table 6, entry 3) or in the presence of TESCl (Table 6, entry 4), in which case, the reduced phosphine would be the dominant promoter rather than the initial phosphine oxide. Even $P(O)Bu_3$, which cannot be reduced to phosphine under these reaction conditions, could bring about the transformation (Table 6, entry 5; Table 5, entry 8), thereby indicating that phosphine oxide with silane could also reduce acid chloride. Although it was reported previously that phosphine can mediate the reduction of acyl

Table 6. Control Experiments To Test the Possibility of Reducing 2a[a]



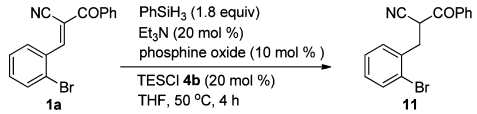
entry	phosphine oxide	temp	time (h)	yield (%)[b]
1		30	6	0[c]
2[d]	**3**	30	4 (24)[e]	1 (22)[e]
3[d]	**3**	50	4	66
4	**3**	50	4	74
5	$(O)PBu_3$	50	4	41

[a]Reaction was carried out using **2a** (0.2 mmol), phosphine oxide (0.2 mmol), phenylsilane (18 equiv), and Et_3N (2 equiv) in dry THF (1.0 mL) under Ar atmosphere. [b]NMR yield. [c]No conversion of **2a**. [d]Without **4b**. [e]NMR yield at corresponding time is shown in parentheses.

chlorides to aldehydes,[9] phosphine oxide could assist in this reduction, which has never been reported to the best of our knowledge. Our optimized conditions (Table 1) ensured that reduction of phosphine oxide **3** was highly efficient, and the generated phosphine was immediately trapped by **1**, thereby preventing reduction of **2** by either **3** or phosphine, thus allowing us to use only 1.1 equiv of **2**.

In the absence of **2**, **1a** was examined for its susceptibility toward reduction under our optimized reaction conditions (Scheme 3). When **3** was employed, no formation of reduced **11**

Scheme 3. Control Experiments To Test Reduction of 1a



1) Phosphine oxide = **3** (89% of **1a** and 10% of phosphorus zwitterion **I**)

2) Phosphine oxide = $P(O)Bu_3$ (77% of **1a** and 10% of **11**)
After 24 h, (<5% of **1a** and 66% of **11**)

was observed due to the efficient reduction of **3** and subsequent generation of expected **I**. In the presence of $P(O)Bu_3$ (which cannot be reduced to PBu_3 under the reaction conditions), **11** was obtained in 10% yield within 4 h. When the reaction was prolonged for 24 h, further reduction of **1a** took place to furnish **11** in 66% yield. This indicates that if the phosphine oxide is not efficiently reduced to phosphine, it can bring about reduction of **1**, which would eventually result in the lower furan adduct yield. Our optimized conditions ensured that TESCl significantly activated **3**, which was efficiently reduced into corresponding phosphine, preventing the reduction of **1**.

A plausible reaction mechanism is proposed in Scheme 4. First, **4b** reacts with the **3** to afford intermediate **II**.[10,12] Reduction of **3** into phosphine by phenylsilane in the presence of Et_3N takes place. Michael addition of phosphine to the Michael acceptor provides the zwitterionic intermediate **I**. Subsequently, **I** undergoes O-acylation with **2** to afford phosphonium chloride **III** and is in situ converted into phosphorus ylide **IV** after deprotonation by Et_3N. Finally, the furan adduct is obtained via intramolecular Wittig reaction with regeneration of **3**. Notably, in addition to **4b** (which participates in the first catalytic turn of phosphine oxide reduction), in situ generated byproduct, Et_3N·HCl, catalyzes the reduction of **3** in the succeeding catalytic turns. Et_3N is regenerated by the elimination of $HCl_{(g)}$ from Et_3N·HCl in THF at increased reaction temperature. The

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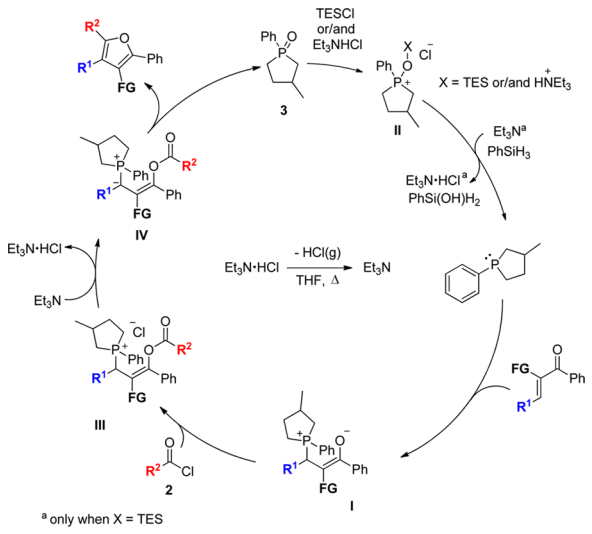
Scheme 4. Plausible Reaction Mechanism in the Presence of Catalytic Amounts of Et_3N, 3, and 4b



success of this catalytic reaction cycle relies on the extent of chemoselectivity accomplished at two stages of the cycle via (i) efficient reduction of **3**, thereby preventing the reduction of **1** and **2** catalyzed by **3**, and (ii) chemoselective addition of generated phosphine onto **1** rather than **2** (Table 6, Scheme 3), leading to efficient generation of furans.

In summary, we developed a novel protocol to synthesize highly functionalized furans utilizing catalytic amounts of phosphine oxide and Et_3N under mild conditions. The concept of recyclable Et_3N was employed for the first time in a catalytic Wittig reaction. An unprecedented activation of phosphine oxide by silyl chloride and $Et_3N{\cdot}HCl$ for its highly chemoselective reduction in the presence of acyl chloride and electron-deficient olefins was achieved. This protocol could prove to be significant on an industrial scale as it averts the need for using stoichiometric amounts of phosphine and base. Related work utilizing other functionalized substrates is underway in our laboratory, and the results will be published in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01781.

Results of the mechanism study, experimental procedures, characterization data, and spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(12) For the detailed experimental study on phosphine oxide reduction, see the Supporting Information.

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