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n-BuLi as a Highly Efficient Precatalyst for Hydrophosphonylation of Aldehydes and Unactivated Ketones

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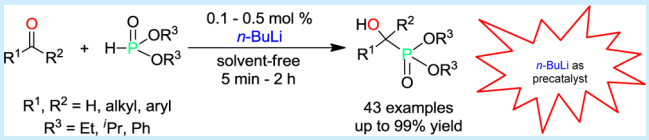
Supporting Information

ABSTRACT: It was found for the first time that organic alkali metal compounds serve as highly efficient precatalysts for the hydrophosphonylation reactions of aldehydes and unactivated ketones with dialkyl phosphite under mild conditions. For ketone substrates, a reversible reaction was observed, and the influence of catalyst loading and reaction temperature on the reaction equilibrium was studied in detail. Overall, the hydrophosphonylation reactions catalyzed by 0.1 mol % *n*-BuLi were completed within 5 min for a broad range of substrates and generated a series of α-hydroxy phosphonates in high yields.



Since organic phosphoric compounds play an important role in organometallic, coordination, and biological chemistry, the corresponding C−P bond formation is fundamentally important in organic synthesis. α-Hydroxy phosphonates, one important type of organic phosphoric compounds, possess intriguing biological activities and have gained widespread applications in many areas, including biological and pharmaceutical industries, due to their physical and structural similarity to biologically important phosphate esters.[1] Thus, the synthesis of α-hydroxy phosphonates has received increasing attention. Despite the numerous methods developed, the most atom-economic and straightforward method is the Pudovic reaction,[2] i.e., the nucleophilic addition of carbonyl compounds with phosphites (also known as hydrophosphonylation reaction). Both racemic[2] and asymmetric[3] α-hydroxy phosphonates are accessible through this strategy. Generally, inorganic and organic bases are popular promoters or catalysts for the Pudovic reaction.[4] However, most of these reactions require stoichiometric or even more bases,[4a−d,f,g,i] high temperatures of 60−70 °C[4d] or microwave irradiation,[4f,i] and reaction times of several hours[4a,b,d,g] in order to obtain decent yields. Moreover, these strategies are largely limited to a narrow scope of substances. They mainly gave satisfactory yields for aldehydes with low yields for ketones.[4a−c,f,i] Some acidic compounds, such as TFA/TfOH,[5] In/HCl,[6] and Ti(O^iPr)$_4$,[7] reportedly mediate the hydrophosphonylation reactions of both aldehydes and ketones to give moderate to high yields with high catalyst loadings and long reaction times. In recent years, significant progress has been achieved in this area. Some organolanthanide complexes reportedly catalyze hydrophosphonylation reactions of aldehydes and ketones with high efficiency at rt under mild conditions (in general 0.1 mol % of catalyst loading and 5−20 min of reaction time).[8] However, in most cases, the synthesis of ligands and corresponding organolanthanide complexes is somewhat tedious and requires multiple steps. Therefore, the development of a highly efficient and easily available catalytic system to synthesize α-hydroxy phosphonate is still meaningful.

Recently, we reported the synthesis of anionic lanthanide amides (2,6-^{i}Pr$_2$PhNH)$_5$LnLi$_2$(THF)$_2$ (Ln = Sm, Nd, Y) stabilized by simple anilido ligands, which are efficient and easily available precatalysts for hydrophosphonylation reactions. 0.1 mol % of (2,6-^{i}Pr$_2$PhNH)$_5$SmLi$_2$(THF)$_2$ catalyzed a quantitative transformation of a range of both aldehydes and ketones.[9] Since these complexes can be considered as additives of (2,6-^{i}Pr$_2$PhNH)$_3$Ln and two equivalents of (2,6-^{i}Pr$_2$PhNH)Li, we were prompted to explore the role of organic alkali metal compounds in hydrophosphonylation reactions. Alkali metal compounds have been reported to promote the addition of phosphorus derivatives on carbonyl compounds.[10] Although organolithium compounds are commonly used as stoichiometric bases in organic synthesis, their application as catalysts has been less explored.[11] It turned out that a series of organolithium compounds are highly efficient precatalysts for hydrophosphonylation reactions of aldehydes and ketones under mild conditions.

The reaction of benzaldehyde with diethyl phosphite was chosen as a model reaction to optimize reaction conditions, and (2,6-^{i}Pr$_2$PhNH)Li (0.2 mol %) was selected as the precatalyst, which is equivalent to 0.1 mol % of the aforementioned complex of (2,6-^{i}Pr$_2$PhNH)$_5$LnLi$_2$(THF)$_2$ in terms of lithium.[9] The reaction proceeded smoothly at rt in neat, and a quantitative yield was achieved within 5 min (Table 1, entry 1). A complete transformation of benzaldehyde to α-hydroxy phosphonate **3a** was also realized even when the amount of (2,6-^{i}Pr$_2$PhNH)Li was decreased to 0.1 mol % (Table 1, entry 2). However, the yield dropped significantly when the catalyst loading was further decreased to 0.05 mol % (Table 1, entry 3), which may be attributed to the extremely sensitive character of (2,6-^{i}Pr$_2$PhNH)Li to a small amount of moisture and impurities in the reaction mixture. A number of organolithium compounds,

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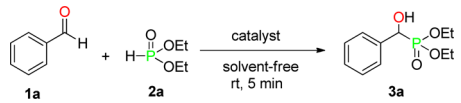
Table 1. Hydrophosphonylation of Benzaldehyde Catalyzed by Organolithium Compounds[a]



1a 2a 3a

entry	cat. (mol %)	yield (%)[b]	TOF (h^{-1})
1	2,6-^{i}Pr$_2$PhNHLi (0.2)	>99	5940
2	2,6-^{i}Pr$_2$PhNHLi (0.1)	>99	11 880
3	2,6-^{i}Pr$_2$PhNHLi (0.05)	86	20 640
4	2,6-Me$_2$PhNHLi (0.1)	>99	11 880
5	PhNHLi (0.1)	>99	11 880
6	(Me$_3$Si)$_2$NLi (0.1)	>99	11 880
7	^{i}Pr$_2$NLi (0.1)	87	10 440
8	*n*-BuLi (0.1)	>99	11 880

[a]Reaction conditions: benzaldehyde **1a** (5.0 mmol), diethyl phosphite **2a** (6.0 mmol), catalyst (required amount), rt, 5 min. [b]Isolated yields.

including 2,6-Me$_2$PhNHLi, PhNHLi, (Me$_3$Si)$_2$NLi, and *n*-BuLi, also efficiently catalyzed this transformation and yielded **3a** in quantitative yields under mild conditions, with the exception of lithium diisopropylamide (LDA) which led to a lower yield of 87% (Table 1, entries 4−8). Due to its easy availability, *n*-BuLi was selected as the precatalyst for further study.

As shown in Figure 1, this catalytic system is applicable to reactions of a variety of aldehydes with diethyl phosphite, and good to excellent isolated yields of 90−99% were achieved under optimized reaction conditions. The electronic properties of aromatic aldehydes do not obviously influence the reaction outcomes. Quantitative yields were obtained for aromatic

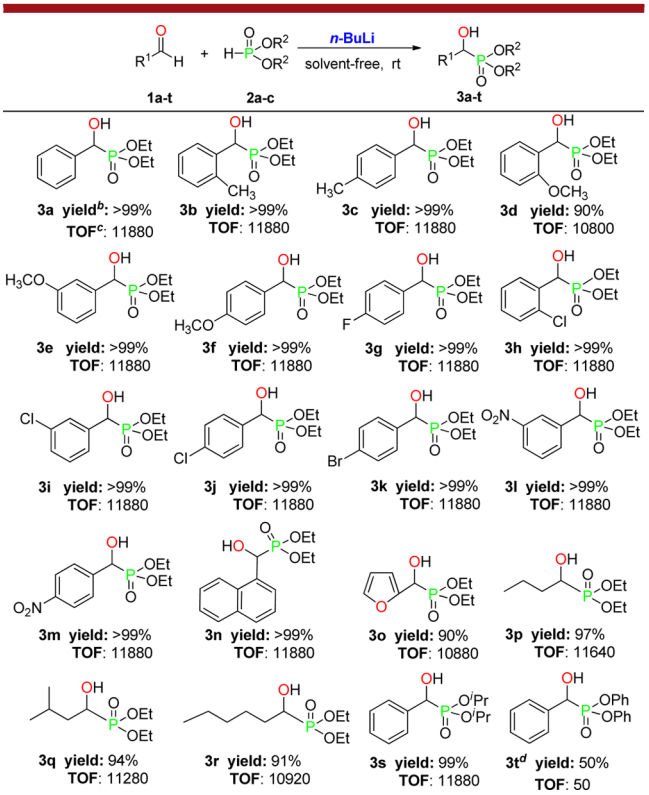


Figure 1. Scope of hydrophosphonylation of aldehydes catalyzed by *n*-BuLi.[a] [a] Reaction conditions: aldehyde (5.0 mmol), phosphite (6.0 mmol), *n*-BuLi (0.1 mol %), rt, 5 min. [b] Isolated yields. [c] h^{-1}. [d] *n*-BuLi (0.5 mol %), 2 h.

aldehydes bearing a substituent at the *para*- or *meta*-position of either an electron-donating group, such as CH_3− (**1c**) and CH_3O− (**1e**, **1f**), or an electron-withdrawing group, such as F− (**1g**), Cl− (**1i**, **1j**), Br− (**1k**), and NO_2− (**1l**, **1m**). Different from reactions catalyzed by organolanthanide complexes,[9] the steric effect in this study is not significant. The reactions proceeded smoothly for aldehydes with CH_3− and Cl− substituents at the *ortho*-position (**1b** and **1h**). However, the catalytic system seems to be more sensitive to the presence of the O atom at the *ortho*-position, and the yield of **3d** decreased slightly to 90% for *p*-methoxybenzaldehyde. Coordination of the OMe group to Li may be responsible for the reduced activity. The reaction with furfural aldehyde is also affected by the O atom in the heterocycle and afforded **3o** in the same yield of 90%. Reaction with 1-naphthaldehyde yielded **3n** in a quantitative yield. Furthermore, both linear and branched aliphatic aldehydes were also expediently converted to the corresponding α-hydroxy phosphonates **3p**−**3r** in 91−97% yields.

Besides diethyl phosphite, hydrophosphonylation reactions of benzaldehyde with different phosphites were also studied (Figure 1). The reaction with diisopropyl phosphite gave rise to the expected product **3s** in 99% yield, while that with diphenyl phosphite afforded **3t** in a lower yield of 50%.

Since the performance of *n*-BuLi is quite promising in catalyzing hydrophosphonylation reactions, the study was further extended to more challenging unactivated ketones. A range of organic alkali metal compounds were tested in the hydrophosphonylation reaction of acetophenone with diethyl phosphite, and in general moderate to good isolated yields were obtained in the presence of 0.1 mol % precatalyst (Table S1, Supporting Information).

Lithium amides bearing either aromatic or aliphatic *N*-substituent were studied, and the corresponding α-hydroxy phosphonate **5a** was isolated in yields of 56−78% (Table S1, entries 1−7). Different alkali metals did not affect the catalytic activity, and **5a** was isolated in similar yields using lithium amide, sodium amide, or potassium amide as the precatalyst (Table S1, entries 1, 8, and 9). *n*-BuLi proved to be one of the best performers by yielding **5a** in 75% yield (Table S1, entry 10). The yield of **5a** dropped dramatically to 28% when the catalyst loading decreased to 0.05 mol % (Table S1, entry 11), which is consistent with the finding with benzaldehyde (*vide supra*). Due to the ease of availability and low cost of *n*-BuLi, it was employed as the precatalyst to further optimize the reaction conditions.

Attempts to improve the yield by increasing the amount of *n*-BuLi failed. In fact, the isolated yield of **5a** decreased from 75% to 21% as the amount of *n*-BuLi increased from 0.1 to 10 mol % (Table 2, entries 1−5). This finding suggests that α-hydroxy phosphonate probably decomposed in the presence of *n*-BuLi, which is consistent with previous reports on other bases that catalyzed/promoted the retro-hydrophosphonylation reaction.[12] Thus, the reversed reaction was investigated in detail by treating **5a** with *n*-BuLi in hexane, and the results are summarized in Table 2 (entries 6−10). It is clear that the retro-hydrophosphonylation reaction did occur in the presence of *n*-BuLi, and the isolated yield of acetophenone increased significantly from 3% to 75% as the loading of *n*-BuLi increased from 0.1 to 10 mol %. Apparently, the amount of base plays a crucial role in the retro-hydrophosphonylation reaction. A relatively low base loading is preferred for the hydrophosphonylation reaction, and a high base loading is advantageous for the retro-hydrophosphonylation reaction. In sharp contrast, no retro-hydrophosphonylation

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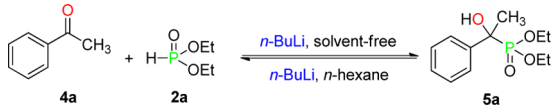
Table 2. Hydrophosphonylation and Retro-hydrophosphonylation Reactions Catalyzed by *n*-BuLi



4a 2a 5a

				yield (%)	
entry	catalyst loading (mol %)	time (min)	temp (°C)	5a[a]	4a[b]
1	0.1	20	25	75	
2	0.5	20	25	59	
3	1.0	20	25	38	
4	5.0	20	25	31	
5	10	20	25	21	
6	0.1	20	25		3
7	0.5	20	25		8
8	1.0	20	25		10
9	5.0	20	25		25
10	10	20	25		75
11	0.1	5	−25	77	
12	0.1	5	−10	88	
13	0.1	5	0	96	
14	0.1	5	10	95	
15	0.1	5	50	63	
16	0.1	5	75	47	

[a]Reaction conditions: acetophenone **4a** (5.0 mmol), diethyl phosphite **2a** (6.0 mmol), *n*-BuLi (required amount). Isolated yields. [b]Reaction conditions: α-hydroxy phosphonates **5a** (5.0 mmol), *n*-BuLi (required amount), *n*-hexane (2 mL). Isolated yields.

reaction of tertiary α-hydroxy phosphonates occurred under identical conditions.

A further study revealed that the reversible reaction of acetophenone with diethyl phosphite reached equilibrium within 5 min at 25 °C with 0.1 mol % *n*-BuLi. The yield of **5a** remained almost unchanged even after the reaction time was prolonged to 120 min (Table S2, entries 1−5, Supporting Information). Besides the catalyst loading, the reaction temperature also plays an important role in influencing the equilibrium of this reversible reaction. An initial increase in the yield, followed by a decrease, was observed when the reaction temperature increased from −25 to 75 °C (Table 2, entries 11−16). The highest yield of 96% was observed at 0 °C (Table 2, entry 13), and a similar yield of 95% was obtained at 10 °C (Table 2, entry 14). However, the yield dropped significantly when the reaction temperature decreased to lower than 0 °C, and the yield of **5a** was only 77% within 5 min at −25 °C (Table 2, entries 11 and 12), which can be attributed to the low reaction rate at low temperatures. Meanwhile, the yield decreased significantly from 77% to 47% when the reaction temperature increased from 25 to 75 °C (Table 2, entries 11, 15, and 16). These results reveal that a relatively low reaction temperature is advantageous for the hydrophosphonylation of acetophenone, whereas a higher reaction temperature is preferred for the retro-hydrophosphonylation reaction, which can be attributed to the fact that the hydrophosphonylation reaction is exothermic, and the retro-hydrophosphonylation reaction is endothermic. Thus, the optimal reaction conditions for ketones are set as follows: 0.1 mol % of *n*-BuLi as the precatalyst, at 10 °C, 5 min reaction time, solvent-free.

Under the optimized conditions, the reactions of various unactivated ketones with diethyl phosphite were examined, and the results are presented in Figure 2.

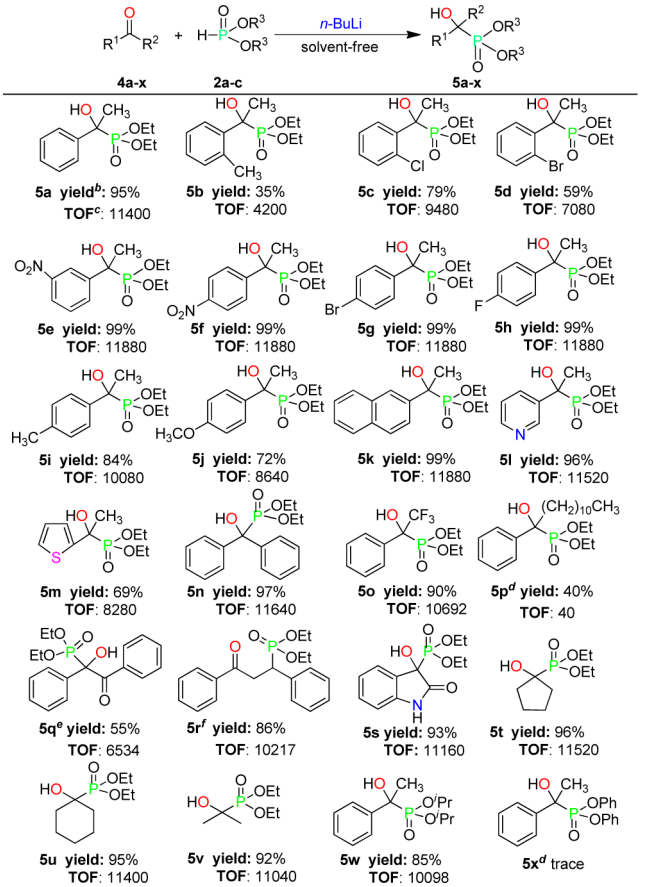


Figure 2. Scope of hydrophosphonylation of ketones catalyzed by *n*-BuLi[a] [a] Reaction conditions: ketone (5.0 mmol), phosphite (6.0 mmol), *n*-BuLi (0.1 mol %), 10 °C, 5 min. [b] Isolated yields. [c] h^{-1}. [d] *n*-BuLi (0.5 mol %), 2 h, rt. [e] Diethyl phosphite (12.0 mmol). [f] Room temperature.

In general, *n*-BuLi efficiently catalyzed the hydrophosphonylation reaction of both aromatic and aliphatic ketones to give quaternary α-hydroxy phosphonates in moderate to excellent yields. The steric effect of ketones is profound, which is different from that of aldehydes (*vide supra*). Aromatic ketones bearing an *ortho*-substitution (CH_3−, Cl−, Br−) on the phenyl ring showed relatively low activity, which afforded the targeted products **5b**, **5c**, and **5d** in yields of 35%, 79%, and 59%, respectively. In comparison with known systems, *n*-BuLi still showed higher activity for *ortho*-substituted ketones. For example, **4c** was converted to **5c** in 52% yield within 2 h catalyzed by $(2,6\text{-}^{i}Pr_2PhNH)_5SmLi_2(THF)_2$.[9] On the other hand, the electronic effect of ketones on the hydrophosphonylation reaction is also obvious. Ketones bearing electron-withdrawing substituents at either *meta*- or *para*-positions, including O_2N−, Br−, and F−, gave the desired products **5e**−**5h** in nearly quantitative yields, respectively. However, the *para*- substituted substrates bearing electron-donating substituents, such as CH_3− and CH_3O−, yielded the products **5i** and **5j** in obviously lower yields of 84% and 72%, respectively. Reaction of 2-acetonaphthone yielded **5k** in a quantitative yield. Ketones bearing heterocyclic substituents such as 3-acetylpyridine and 2-acetylthiophene were converted to the corresponding α-hydroxy phosphonates **5l** and **5m** in 96% and 69% yield, respectively.

In addition to methyl ketones, other aryl and aliphatic ketones were also tested in this transformation. The reaction with bulky benzophenone proceeded smoothly and yielded **5n** in 97% yield.

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2,2,2-Trifluoroacetophenone reacted with diethyl phosphite and gave rise to fluorine-containing phosphonate **5o** in 90% yield, which is a precursor to a serine esterase inhibitor.[13] Dodecanophenone was transformed to the expected product **5p** in a moderate yield of 40%. The reaction with benzil led to the isolation of **5q** in 55% yield, with the addition occurring to one carbonyl group, despite the presence of 2.4 equiv of phosphite. 1,4-Addition instead of 1,2-addition occurred selectively to chalcone, which yielded the product **5r** in 86% yield. Xu et al. reported that the reaction catalyzed by a lanthanide−lithium complex formed 2-oxido-1,2-oxaphospholane after a sequential phospha-Michael/Pudovik reaction, which was not detected in this case.[8h]

It should be noted that, for isatin with the carbonyl group incorporated in the heterocyclic ring, *n*-BuLi proved to be a suitable precatalyst to produce *α*-hydroxy phosphonate **5s** in 93% yield. Furthermore, linear and cyclic aliphatic ketones were also applicable to this system, and the corresponding products **5t**−**5v** were isolated in excellent yields of 92−96%.

The hydrophosphonylation reactions of different phosphites with acetophenone were also studied. Diisopropyl phosphite reacted straightforwardly and gave rise to **5w** in 85% yield. However, *n*-BuLi proved to be limited in catalyzing the reaction of diphenyl phosphite and only led to a trace amount yield.

In conclusion, an easily available and inexpensive organometallic compound *n*-BuLi was found to be a highly efficient single-component catalyst for the hydrophosphonylation reaction of aldehydes and unactivated ketones. Under mild conditions, this strategy gives *α*-hydroxy phosphonates in generally good to excellent yields. Moreover, *n*-BuLi is capable of catalyzing both directions of the reversible Pudovik reaction of ketones, and the amount of *n*-BuLi as well as reaction temperature play crucial roles in the reaction equilibrium. Furthermore, this system features wide substrate scopes and mild reaction conditions (e.g., low catalyst loading, short reaction time), which makes it the simplest and most efficient strategy for *α*-hydroxy phosphonate synthesis. Study is ongoing in our laboratory to extend this system to other transformations.

■ ASSOCIATED CONTENT

Supporting Information

General procedure; Tables S1, S2; and characterizations of *α*-hydroxyphosphonates. These materials are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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