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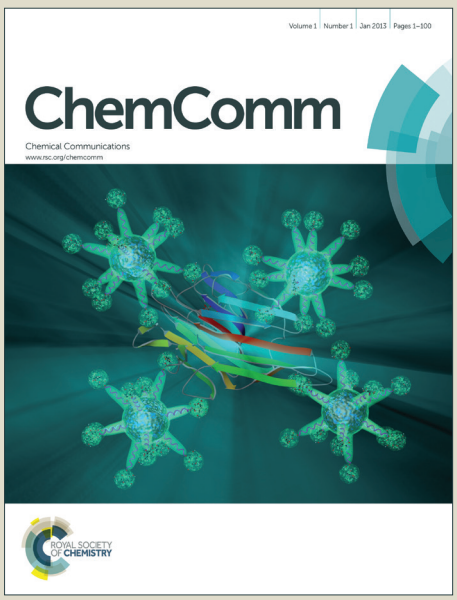

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H-phosphonate-mediated sulfonylation of heteroaromatic *N*-oxides: a mild and metal-free one-pot synthesis of 2-sulfonyl quinolines/pyridines

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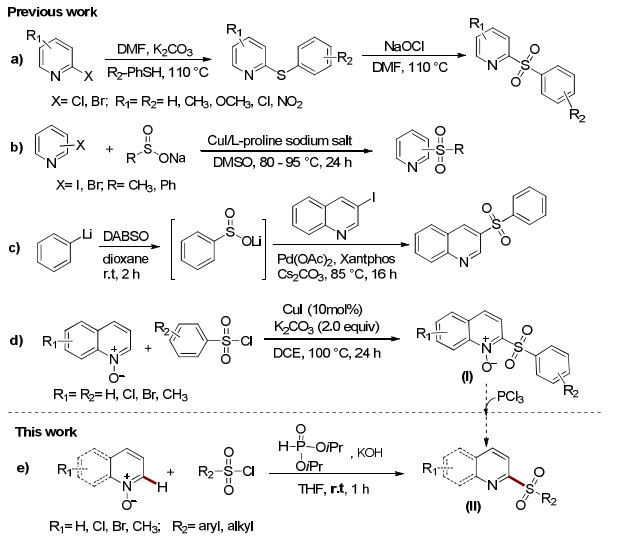
A smart *H*-phosphonate-mediated synthetic strategy for the sulfonylation of heteroaromatic *N*-oxides has been developed, by which a large variety of 2-sulfonyl quinolines/pyridines were synthesized starting from easily available sulfonyl chlorides, diisopropyl *H*-phosphonate and pyridine/quinoline *N*-oxides in one pot under metal-free conditions at room temperature.

The possibility of direct introduction of a new functionality via direct C-H bond transformation is a highly attractive strategy with high atom economy in covalent synthesis.[1] Substantial growth in carbon-heteroatom bond formation based on the transition-metal-catalyzed C-H bond activation has been observed.[2] It is especially worth emphasizing that nearly all the reported methods employed metal, noble metal or even toxic metal catalysts for C-H bond activation reactions.[3] However, from environmental and economic views, metal-free chemistry should be greatly encouraged.[4] It is worth noting that the development of effective C-S bond formation reactions via direct C-H activation is under developed compared to C-N[5] and C-O[6] bond formation. It is well known that, as an extremely important structural moiety, quinoline (or pyridine) moiety exists in a wide range of pharmaceutical interest products.[7] However, it has been found that quinine, a naturally occurring product for treatment of malaria, is easily detoxified in the body by oxidation to the 2-hydroxy derivative which has much less therapeutic activity. So lots of synthetic methods have been focused on introducing groups into the 2-position in order to block this mode of detoxification.[8] Sulfones are not only versatile synthetic intermediates, but also exhibit broad range of physical, chemical and biological activities. They play an especially important role in agricultural, industrial and pharmaceutical chemistry.[9] Therefore, a rapid, efficient, and practical access to those heteroaromatic sulfone compounds via C-H activation under metal-free conditions is highly desired from a synthetic practicality viewpoint.

In the last decade, several processes for the sulfonylation of these heteroaromatic compounds have been developed as shown in Scheme 1. Traditionally, sulfones are synthesized either by oxidation of the corresponding sulfides[10] as in the case of Scheme 1a[11], or by alkylation or arylation of sulfinate salts[12] as in the cases of Scheme 1b-c[9,13]. However, these traditional methods shown in Scheme 1a-c have associated limitations. For the oxidation method shown in Scheme 1a, the ultimate starting materials are foul-smelling benzenethoils and halopyridines. Halopyridines usually are not commercially available and are problematic to prepare. The arylation of sulfinate salts shown in Scheme 1b-c is achieved by coupling reactions of halopyridines/quinoline with sulfinate salts under metal catalytic conditions. However, both halopyridines/quinolines and sulfinate salts have very limited commercial availability. In particular, sulfinate salts are often prepared from the corresponding sulfonyl chlorides.[14] Recently,



Scheme 1. Comparison of previous work with this work

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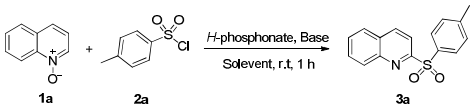
Cui's group developed a protocol to synthesize 2-(aryl sulfonyl)quinoline *N*-oxides in chemo- and regioselective manners via copper-catalyzed C-H bond activation, starting from quinoline *N*-oxides and sulfonyl chlorides (Scheme 1d).[15] Although this introduction of a new functionality via copper-catalyzed C-H bond activation of quinoline *N*-oxides is an attractive strategy, nevertheless, it required metal catalyst, a relatively high temperature, and a rather long reaction time (24 h) to progress to reaction. Moreover, PCl_3, a harsh reagent, would usually be used if one wanted to reduce the 2-(aryl sulfonyl)quinoline *N*-oxides (Scheme 1d-I) to the corresponding 2-(aryl sulfonyl)quinolines (Scheme 1e-II).[16] Herein, we disclose a highly efficient one-pot procedure to build a large variety of both 2-(aryl/alkyl sulfonyl)pyridines and 2-(aryl/alkyl sulfonyl)quinolines, via a direct C-H functionalization of pyridine/quinoline *N*-oxides with *H*-phosphonates under metal-free conditions (Scheme 1e). In a sharp contrast to Cui's method, the prominent advantages of our one-pot method include a much reduced reaction time (1 h), a relatively wide scope of reactants, metal free and room temperature reaction conditions, and a one-step procedure to the final sulfonyl pyridines/quinolines.

We initiated the meaningful study, starting with establishing optimal experimental conditions using the model reaction of quinoline *N*-oxide (**1a**) with TsCl (**2a**) in the presence of dialkyl *H*-phosphonates under open-air conditions for 1 h at room temperature, as summarized in Table 1. The influence of a variety of dialkyl *H*-phosphonates on the model reaction was investigated (entries 1-5). A high yield of **3a** was obtained when diisopropyl *H*-phosphonate was employed (85%) (entry 2). The ideal amount of diisopropyl *H*-phosphonate was then explored (entries 2 and 6-10). The reaction did not proceed in the absence of any dialkyl *H*-phosphonate (entry 6). The yield increased from 43% to 85% as the amount of diisopropyl *H*-phosphonate increased from 0.5 to 1 equiv. (entries 7-8, 2), and decreased from 85% to 80% as the amount continuously increased from 1 to 1.5 equiv (entries 2, 9-10). The ideal amount of TsCl was also explored. It was found that the yield increased from 45% to 85% with the increase of TsCl from 1 equiv to 2 equiv (entries 11-12, 2). However the yield began to decrease when the amount was above 2 equiv. (entry 13). Further investigation into the influence of various bases on the reaction was carried out (entries 2 and 14-18). Without base no product was formed (entry 18). The use of KOH brought about a highest yield (85%) (Table 1, Entry 2), whereas the other bases resulted in relatively low yields of **3a**: i.e., K_2CO_3 (trace), *t*-BuOK (43%), Et_3N (53%), Et_2NH (28%) (entries 14-17). The investigation on the optimal amount of KOH (Table 1, entries 2 and 19-22) indicated that 4 equiv of KOH (entry 2) was an appropriate amount. Further screening of the solvents showed that THF was the best choice among those tested solvents (entries 4 and 23–29). By the way, the reason why the yield was so low in dioxane (Table 1, entry 23), and why the yield was so high when the reaction was performed in ethanol (Table 1, entry 26) were further explored (For the reason, along with supplemental experiments, see supporting information). Therefore, the best yield of **3a** (85%) was obtained by employing 1 equiv diisopropyl *H*-phosphonate, 2 equiv TsCl, 4 equiv KOH in THF (entry 2).

Table 1. Optimization of reaction conditions[a]

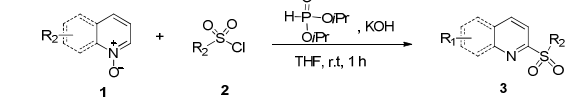


1a 2a 3a

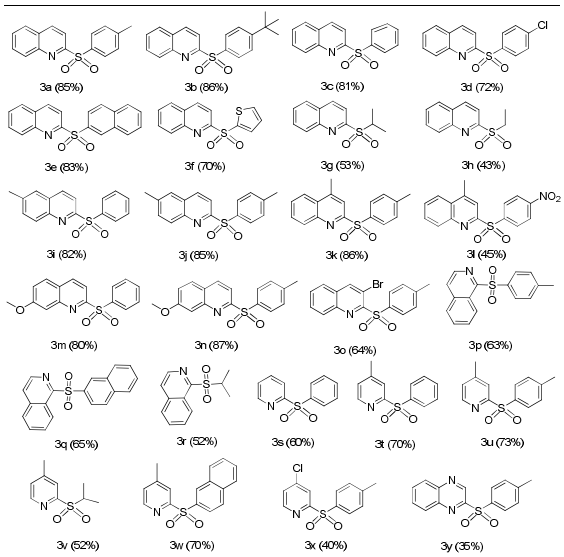
Entry	*H*-phosphonate ($HPO(OR)_2$,R=)(equiv)	2a (equiv)	Base(equiv)	Solvent	Yield(%)[b]
1	CH_2CH_3 (1)	2	KOH(4)	THF	83
2	**$CH(CH_3)_2$(1)**	**2**	**KOH(4)**	**THF**	**85**
3	$CH_2CH_2CH_3$(1)	2	KOH(4)	THF	75
4	Ph(1)	2	KOH(4)	THF	73
5	CH_2Ph(1)	2	KOH(4)	THF	62
6	----	2	KOH(4)	THF	0
7	$CH(CH_3)_2$(0.5)	2	KOH(4)	THF	43
8	$CH(CH_3)_2$(0.75)	2	KOH(4)	THF	67
9	$CH(CH_3)_2$(1.25)	2	KOH(4)	THF	82
10	$CH(CH_3)_2$(1.5)	2	KOH(4)	THF	80
11	$CH(CH_3)_2$(1)	1	KOH(4)	THF	45
12	$CH(CH_3)_2$(1)	1.5	KOH(4)	THF	67
13	$CH(CH_3)_2$(1)	2.5	KOH(4)	THF	84
14	$CH(CH_3)_2$(1)	2	K_2CO_3(4)	THF	trace
15	$CH(CH_3)_2$(1)	2	*t*-BuOK(4)	THF	43
16	$CH(CH_3)_2$(1)	2	Et_3N(4)	THF	53
17	$CH(CH_3)_2$(1)	2	Et_2NH(4)	THF	38
18	$CH(CH_3)_2$(1)	2	----	THF	0
19	$CH(CH_3)_2$(1)	2	KOH(1)	THF	trace
20	$CH(CH_3)_2$(1)	2	KOH(2)	THF	25
21	$CH(CH_3)_2$(1)	2	KOH(3)	THF	65
22	$CH(CH_3)_2$(1)	2	KOH(5)	THF	81
23	$CH(CH_3)_2$(1)	2	KOH(4)	1,4-dioxane	trace
24	$CH(CH_3)_2$(1)	2	KOH(4)	DMSO	0
25	$CH(CH_3)_2$(1)	2	KOH(4)	DMF	0
26	$CH(CH_3)_2$(1)	2	KOH(4)	ethanol	80
27	$CH(CH_3)_2$(1)	2	KOH(4)	acetone	25
28	$CH(CH_3)_2$(1)	2	KOH(4)	CH_3CN	81
29	$CH(CH_3)_2$(1)	2	KOH(4)	toluene	30

[a] Reaction conditions: 0.2 mmol of 1a, 0.2-0.4 mmol of 2a, *H*-phosphonate (equiv), base and 7 mL of solvent in a 25 mL round-bottom flask at room temperature for 1 h. [b] Isolated yields.

Table 2. Scope of the sulfonylated quinoline and related derivatives



1 2 3



Reaction conditions: 0.2 mmol of 1, 0.4 mmol of 2, diisopropyl *H*-phosphonate (1.0 equiv), KOH (4.0 equiv) and 7 mL of THF in a 25 mL round-bottom flask at room temperature for 1 h.

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With the optimized reaction conditions in hand, we then examined the substrate scope of quinoline *N*-oxides and sulfonyl chlorides. The results were summarized in Table 2. As it can be seen, a variety of aryl sulfonyl chlorides reacted well with quinoline *N*-oxide itself, giving the resulting 2-(aryl sulfonyl)quinolines (**3a-f**) in good yields. Two alkyl sulfonyl chlorides also reacted well with quinoline *N*-oxide to afford the resulting 2-(alkyl sulfonyl)quinolines (**3g-h**) in moderate yields. A series of substituted quinoline *N*-oxides were tested as well, giving the corresponding products (**3i-o**) in good yields. To our delight, the sulfonyl method could further be applied to isoquinoline *N*-oxide, regioselectively producing three corresponding products (**3p-r**). It's especially worth mentioning here that pyridine *N*-oxide and its substituted derivatives, and even quinoxaline *N*-oxide (an aromatic ring with two heteroatoms) smoothly went sulfonylation at the 2-position (**3s-y**). It can be seen that both the electron-donating and -withdrawing groups of sulfonyl chlorides and aromatic *N*-oxides were well compatible to afford the desired products under the optimal reaction conditions. Generally, the reaction efficiency was slightly sensitive to the electronic property. The electron-donating (CH_3, $C(CH_3)_3$) groups on the phenyl ring of sulfonyl chlorides, compared to electron-withdrawing groups (Cl, NO_2) on the ring, gave relatively higher yields as in the cases of **3a-b, d, l**. The electron-donating groups (CH_3, OCH_3) attached to aromatic *N*-oxides led usually to higher yields than did the electron-withdrawing groups (Br, Cl), as in the cases of **3n** and **3o**, **3u** and **3x**.

Dialkyl *H*-phosphonates play a predominant role in organophosphorus chemistry, since as important intermediates, they are frequently employed to synthesize a large variety of bioactive phosphorus-containing products.[17] In order to know what role dialkyl *H*-phosphonate played here in the reaction, the whole reaction process was monitored by ^{31}P NMR every 5 min. (Figure 1). Beginning with diisopropyl *H*-phosphonate **1**, the phosphorus-containing intermediates and product, diisopropyl chlorophosphate **2**, diisopropylphosphate **3** and tetraisopropyl diphosphate **4**, were all well tracked in the proper sequence as shown in Figure 1. A plausible mechanism is proposed accordingly in Scheme 2. Dialkyl *H*-phosphonates often exist in rapid equilibrium with a tautomeric form known as tricoordinated phosphorus form and tetracoordinated form, as in the case of **1'** and **1** shown in Scheme 2.[17c] Diisopropyl phosphite **1'** initially acts as nucleophile to attack the sulfur atom of sulfonyl chloride **5**, and then the reaction

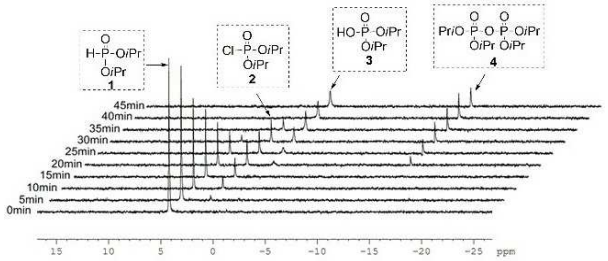
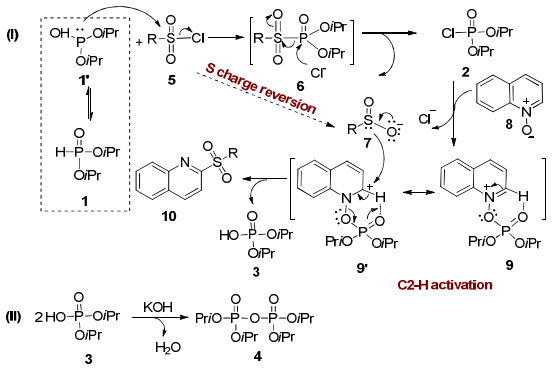


Figure 1: ^{31}P NMR stacks diagram. Reaction conditions: quinoline *N*-oxide (0.2 mmol), TsCl (0.4 mmol), diisopropyl *H*-phosphonate (0.2 mmol) and KOH (0.8 mmol) in THF (7 mL) at room temperature for 1 h. The whole process was monitored by ^{31}P NMR every 5 min (comp-1, 4.07 ppm, comp-2, 1.27 ppm, comp-3, -1.08 ppm, comp-4, -14.42 ppm).



Scheme 2. Proposed reaction mechanism

undergoes a nucleophilic addition and elimination reaction, forming an instable intermediate **6** and a chloride anion. The S-P bond of **6** is weak owing to the strong electron withdrawing abilities of the sulfonyl group and phosphoryl group at two sides of the bond. Subsequently, the chloride anion quickly attacks the phosphorus atom of **6**, via an addition-elimination process, forming diisopropyl chlorophosphate **2** along with sulfonyl anion **7**. It can clearly be seen that the sulfur in **5** is positively charged, whereas the sulfur in **7** is negatively charged. It is to say that, by reacting with dialkyl *H*-phosphonate (**1** or **1'**), sulfonyl chloride **5**, which initially acts as electrophile, can quickly be transformed into nucleophile sulfonyl anion **7** (S charge reversion process). Then, the oxygen atom of quinoline *N*-oxide **8** attacks the phosphorus atom of **2** and triggers another addition-elimination process. A chloride anion is expelled and intermediate **9** is formed. Meanwhile an energetically favorable six-membered ring is generated inside **9** owing to the formation of an intramolecular hydrogen bond**,** by which the covalent C2-H of **9** is effectively activated. It can be seen that **9** is in resonance with **9'**. Then sulfonyl anion **7**, acting as a nucleophile, attacks the carbon 2 of **9'**, initiating an energetically favorable elimination of diisopropyl phosphate **3** along with the formation of the target product **10**. By the way, tetraisopropyl diphosphate **4** is formed via intermolecular dehydration of **3** under basic reaction condition.

Based on the above mechanism, we proposed another new synthetic strategy (Scheme 3), by which a group of 2-sulfonylated quinolines were efficiently synthesized. The related mechanism is shown in Scheme 3. Based on the well-known Atherton-Todd reaction[18], diisopropyl *H*-phosphate **1** can initially be converted into dialkyl chlorophosphate **2** in the presence of carbon tetrachloride and base (Scheme 3). Afterwards, following exactly the same steps as described in Scheme 2, the final product **10** was successfully obtained. The success of this synthetic method gave us a further support for the mechanism shown in Scheme 2. Quite like the first method, this reaction was also performed at room temperature in short reaction time under metal-free conditions. However, the first synthetic strategy shown in Table 2 owns an obvious advantage over this one here shown in Scheme 3 in that it employed wildly available sulfonyl chlorides, rather than sulfinate salts, as sulfonylation agents. As mentioned at the beginning, sulfinate salts currently have very limited commercial availability and are often prepared from sulfonyl chlorides.[14]

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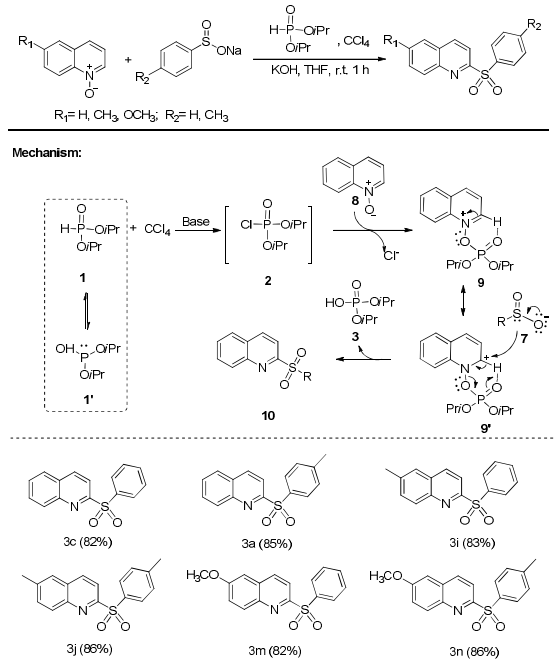

Reaction conditions: quinoline *N*-oxides (1 mmol), sulfonate salts (1 mmol), diisopropyl *H*-phosphonate (1 mmol), KOH (4 mmol) and CCl_4 (0.5 mL) in THF (15 mL) at room temperature for 1 h.

Scheme 3. A new synthetic strategy toward 2-sulfonyl quinolones

In conclusion, we have developed a straight forward method by which a wide variety of *N*-heteroaromatic sulfones were synthesized by a one-pot reaction of pyridine/quinoline *N*-oxides with sulfonyl chlorides in the presence of diisopropyl *H*-phosphonate for 1 h at room temperature. The study on the mechanism indicates that sulfonyl chlorides (electrophile) can be transformed into sulfonyl anions (nucleophile) in the presence of dialkyl *H*-phosphonates. Meanwhile, dialkyl *H*-phosphonates can be transformed into dialkyl chlorophosphates (strong electrophile), which then could, in the following step, react with quinoline/pyridine *N*-oxides to form complexes. By the six-membered ring formed inside the complexes, C2-H of *N*-heteroaromatic substrates could therefore be greatly activated. These key reaction steps make it possible to directly employ wildly available sulfonyl chlorides and aromatic *N*-oxides to synthesize a large variety of *N*-heteroaromatic sulfones under mild and metal-free reaction conditions. The current substrate scope encompasses a wide range of heteroaromatic *N*-oxides, including pyridine *N*-oxides, quinoline *N*-oxides and quinoxaline *N*-oxide, as well as a variety of sulfonyl chlorides, including aryl and alkyl sulfonyl chlorides. Compared with literature methods, great advantages of this strategy include a wide range of reaction substrates, an efficient time-saving one-pot procedure, extremely mild and metal-free reaction conditions. The method will undoubtedly be a far superior alternative for the synthesis of a variety of biologically and chemically significant *N*-heteroaromatic sulfones. Further studies on the applications of this strategy will be reported in due course.

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