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COMMUNICATION

(E)-Specific Direct Julia-Olefination of Aryl Alcohols without Extra Reducing Agents Promoted by Bases

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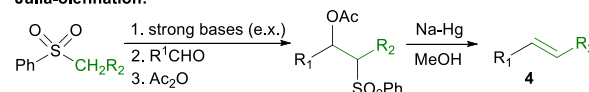
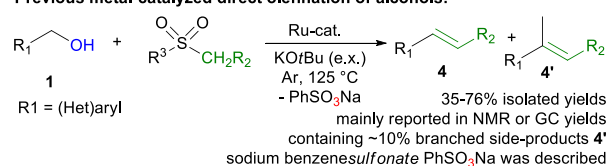
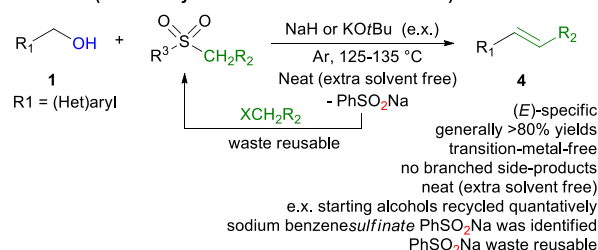
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An unprecedented base promoted direct olefination of aryl alcohols with sulfones via a Julia-type reaction has been described. No extra reductants are needed for Julia reaction since alcohols work as double sources of aldehydes and the hydride. Generally high yields were given for both terminal and highly (E)-selective internal olefins.

The Olefination is one of the most important C=C bond formation reactions¹ since olefins are very important feedstocks or intermediates in both industry and laboratory. Despite numerous methods have been developed to construct C=C bonds, the olefination of carbonyl compounds, such as Wittig reaction;²⁻³ Horner-Wadsworth-Emmons reaction,⁴ Peterson olefination,⁵ Julia olefination (Scheme 1, top),⁶ Tebbe olefination,⁷ dominates the main approaches of olefination in organic synthesis. Recently, the olefination of alcohols *via* a Wittig-type reaction of in situ generated carbonyl compounds has been accomplished by the one-pot oxidation-olefination process catalyzed by palladium-rhodium, copper, ruthenium, or nickel.⁸ Nevertheless, the direct olefination of alcohols *via* either Julia-type or Wittig-type reaction have been barely reported. Until near recently, Milstein and co-workers first reported a powerful method of one-step strategy for the olefination of alcohols with sulfones catalyzed by pincer PNN ruthenium complexes.⁹ In that work, various aryl methanols could give the terminal alkenes in moderate yields (Scheme 1, middle).

Bases such as *t*BuOK and NaH proved sometimes to be crucial in either metal-free or metal catalyzed oxidative-reductive coupling of alcohols and coupling reactions.¹⁰⁻¹² During the course of our work on the base promoted direct amination of alcohols *via* a self-hydride transferring strategy, it was found that in the presence of bases such as NaH or *t*BuONa, the reaction of benzyl alcohol **1a** and phenyl methyl sulfone **2a** could afford styrene in high yields (Scheme 1, bottom). In this work, the branched side-products¹³ such as 1-methyl styrenes were not observed. Various bases were then investigated (Table 1). Without base there was no conversion of **1a** (Entry 1). The bases such as *t*BuONa, *t*BuOK, NaH and KOH gave higher conversions. Excess base is necessary for the deprotonation of sulfone

2a, thus 0.5 equiv of NaH gave rise to a dramatic drop of the conversion from 87% to 33% (Entry 9). Dimethyl sulfone **2b** afforded a slightly lower conversion compared to that of **2a** (Entry 12), while Wittig reagent **2c** gave only 28% conversion (Entry 13). The reaction under air atmosphere resulted in a slight drop of conversion (Entry 14). Thus the conditions described in entry 10 was chosen as the standard conditions.

Julia-olefination:**Previous metal-catalyzed direct olefination of alcohols:****This work (base-catalyzed direct olefination of alcohols):**

Scheme 1.

Next, various alcohols were investigated to test the scope of this method. Aryl methanols reacted with PhSO₂Me **2a** in the presence of NaH and the desired olefins were afforded without side-products. Excess **1a** could be recycled in 90%. For terminal olefins listed in Table 2, generally high isolated yields were given after careful purification on silica gel column despite the styrene products are

normally volatile. For example, styrene **3a** was achieved in 87% yield. The olefin bearing a heterocycle such as **3b** was obtained in 84% yield. Other substituents such as methoxyl (**3d** and **3f**), trifluoromethyl (**3i**), bromo (**3j**), or other groups on phenyl groups were all tolerable under the reaction conditions.

For the internal olefins, the standard reaction conditions were employed with phenyl alkyl sulfones **2d-2f** instead of **2a** (Table 3). Various aryl methanols and sulfones were investigated and the corresponding internal olefins **4** were isolated in generally good to high yields. The olefination is highly *E/Z*-selective and in all cases only (*E*)-isomers were obtained. When PhSO₂CH₂Ph **2d** was subjected to the reaction conditions with benzyl alcohol **1a**, *trans*-stilbene **4a** was isolated in 90% yield. Other substituted stilbenes (**4b** and **4c**) or styryl heterocycles (**4d** and **4e**) could be achieved from **2d** in high yields as well. The direct olefination of cinnamic alcohol with **2d** afforded diene **4g** in 58% yield. PhSO₂Et **2e** and PhSO₂CH₂Py **2f** gave corresponding internal (*E*)-olefins **4i**, **4h-4l** in good to high yields.

Table 1. Screening Reaction Conditions^a

Entry	Base(equiv)	2	T/°C	t/h	3a (%) ^b
1	—	2a	130	24	0
2	<i>t</i> BuONa (1.5)	2a	130	24	70
3	NaH (1.5)	2a	130	24	78
4	<i>t</i> BuOK (1.5)	2a	130	24	71
5	MeONa (1.5)	2a	130	24	40
6	KOH (1.5)	2a	130	24	68
7	<i>n</i> BuLi (1.5)	2a	130	24	30
8	LiHMDS (1.5)	2a	130	24	10
9	NaH (0.5)	2a	130	24	33
10	NaH (1.0)	2a	130	24	71
11	NaH (2.5)	2a	135	5	87 ^c
12	NaH (2.5)	2b	135	5	71
13	NaH (2.5)	2c	135	5	28
14 ^d	NaH (2.5)	2a	135	5	75

^a Conditions: **1a** (1 mL), **2** (1 mmol), base (0.5-2.5 mmol), 130 or 135 °C, argon. All bases and solvents were tested by ICP-AES for trace transition metals (*e.g.*, Ru, Rh, Ir, Pd, Pt, Cu, Fe: not detected in NaH or reaction mixture). See Supporting Information. ^b Determined by ¹H NMR (400 MHz) using 1,4-dioxane and DMSO as internal standards. ^c Excess starting material **1a** was recovered quantitatively. ^d Under air (PhCHO: 0.04 mmol after reaction).

The effects of the amount of base (NaH) and sulfone (PhSO₂Me) were investigated kinetically. The homogeneous reaction solution was monitored by ¹H NMR under standard reaction conditions. A linear dependence of the initial rate on the amount of NaH was observed (Fig. 1A), while that was a zeroth dependence on the amount PhSO₂Me (Fig. 1B). The deuterium labeling experiment demonstrated a first order KIE, indicating a rate-determining step of the C-H bond cleavage (Scheme 2).

A possible mechanism was proposed in Scheme 4. First, trace benzaldehyde **5a** formed *via* a thermal dehydrogenation of **1a** (Scheme 3, Eq. 1),¹⁴ followed by the addition of sulfone salt **2a**-Na to form intermediate **6a**-Na. Sulfone alcohol **6a** could be isolated and was treated either in the presence or absence of alcohol **1a**,¹⁵ but only the reaction with **1a** gave 91% of olefin **3a** (Scheme 3, Eq. 2), indicating that alcohol **1a** is necessary for liberating olefin **3a**. Mainly PhSO₂Na **7** was observed in the immediate ¹H NMR test of the reaction mixture, while after work-up, both **7** and PhSO₃Na **8** could be isolated. The treatment of **8** with **1a** under olefination conditions gave no **7**, while the exposure of **7** in air resulted the oxidation of **7** to **8**, indicating that sodium benzenesulfinate **7** is the final form of sulfone **2a**. Thus a reaction cycle including **6a**-Na, **6a**'-Na, **9**, **10**, and

5a was proposed. Despite intermediates **9** and **10** have not been observed in the reaction yet,¹⁶ the treatments of **9** and **10** under reaction conditions could give styrene **3a** in good to high yields (Scheme 3, Eqs 4 and 5).¹⁷ Key intermediate **5a** might regenerate *via* hydride transferring reduce of **9** by **1a**.¹⁸

Table 2. Terminal Olefins Direct from Alcohols^a

1	2a	3
3a (5 h, 87%)	3b (9.5 h, 84%)	3c (7.5 h, 88%)
3d (7 h, 85%)	3e (10 h, 99%)	3f (24 h, 95%)
3g (10 h, 79%)	3h (36 h, 75%)	3i (19 h, 52%)
3j (15 h, 81%)	3k (15 h, 77%)	3l (17 h, 60%)
3m (23 h, 92%)	3n (20 h, 56%)	3o (12 h, 95%)

^a Conditions: **2a** (1 mmol), **1** (1 mL), NaH (2.5 mmol), 135 °C, argon, isolated yield. The excess alcohols could be recycled quantitatively (see Supporting Information for details).

Table 3. Internal Olefins Direct from Alcohol^a

1	2d-f	4
4a (27 h, 90%)	4b (42 h, 93%)	4c (28 h, 90%)
4d (24 h, 82%)	4e (27 h, 95%)	4f (16 h, 95%)
4g (47 h, 58%)	4h (19 h, 59%)	4i (16 h, 95%)
4j (27 h, 75%)	4k (28 h, 95%)	4l (16 h, 95%)

^a Conditions: **2d-f** (1 mmol), **1** (1 mL), NaH (2.5 mmol), 135 °C, argon, isolated yield. The excess alcohols could be recycled quantitatively (see Supporting Information for details).

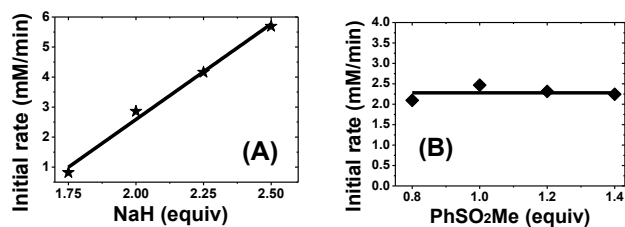
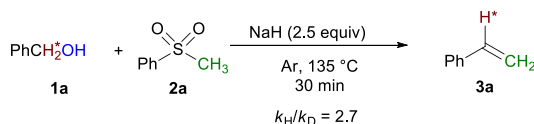
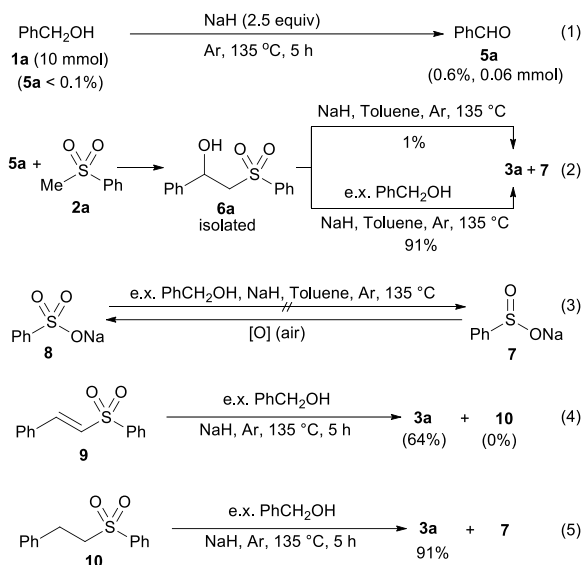


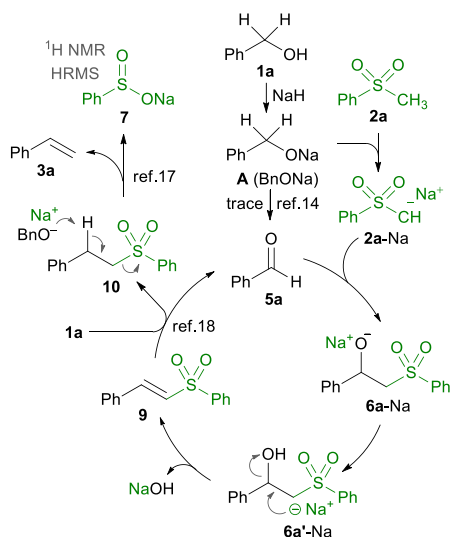
Figure 1. Dependence of the initial rate on (A) NaH and (B) PhSO₂Me.



Scheme 2. Kinetic Isotope Effects.



Scheme 3. Controlled Experiments.



Scheme 4. Proposed Mechanism: Self-Hydride Transferring Redox Process.

Conclusions

In conclusion, a base promoted direct olefination of aryl alcohols with sulfones *via* a Julia-type reaction has been established. This transition metal free process avoids the side reactions such as dehydrogenative oxidation of alcohols, formation of branched styrenes and hydrogenation of olefin products by liberated hydrogen. High (*E*)-selectivity provides a highly efficient access to internal (*E*)-olefins. Non-toxic process, simple reaction conditions, the cheap base reagents, as well as the recycling and reuse of sulfinate waste are all the highlights of this method.

Notes and references

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