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Hydrofunctionalization of alkenols triggered by the addition of diverse radicals to unactivated alkenes and subsequent remote hydrogen atom translocation†

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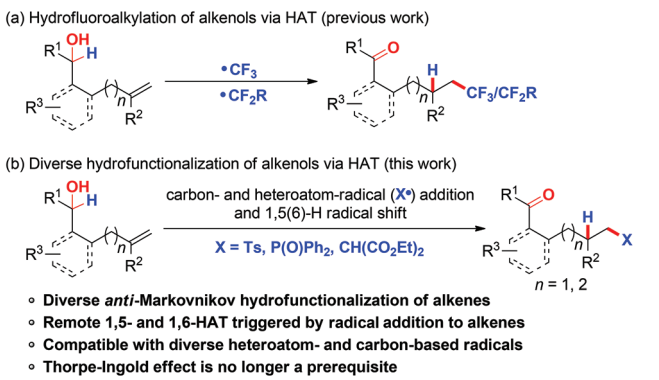
Diverse *anti*-Markovnikov hydrofunctionalization of alkenols triggered by the addition of *S*-, *P*-, and *C*-centered radicals to alkenes followed by intramolecular 1,5(6)-hydrogen atom transfer (HAT) with remote α-C–H bonds of alcohols has been developed. The strategy simultaneously realized the hydrofunctionalization of alkenes and remote alcohol oxidation. This mild and versatile method allows for direct access to valuable sulfonyl-, phosphonyl-, and malonate-substituted ketones or aldehydes from a wide range of alkenols.

Introduction

The hydrofunctionalization of alkenes provides a facile access to a wide range of functionalized alkanes.[1] Among intensive research in this area, the radical-mediated alkene hydrofunctionalization initiated by the addition of radicals to alkenes followed by trapping of the incipient radical with a hydrogen donor represents an efficient and powerful tool for alkene hydrofunctionalization in an *anti*-Markovnikov manner.[2] The use of efficient hydrogen donors is critical for the realization of alkene hydrofunctionalization because of the high propensity of alkyl radical intermediates, particularly for linear alkene substrates, to undergo undesired competitive pathways such as 1,2-difunctionalization and β-hydrogen elimination.[3] Compared with the well-established external hydrogen donors, intramolecular hydrogen delivery *via* 1,*n*-hydrogen atom transfer (HAT) for hydrofunctionalization of unactivated alkenes has recently attracted considerable attention due to its high regio-selectivity and concomitant remote C–H bond functionalization.[4] In this respect, our group and others have independently reported the general and efficient hydrofluoroalkylation of alkenes with suitably positioned alcohols/ethers as internal hydrogen donors to afford a variety of fluoroalkyl-containing carbonyl products (Scheme 1a).[5] However, the research on this chemistry was confined to fluoro-containing radical sources, which unnecessarily limited both the scope and the potential of this method for practical applications. Hence, the realization of hydrofunctionalization of alkenols *via* this strategy with diverse heteroatom- or carbon-centered radical sources is highly desirable.

Organosulfones and organophosphorus compounds are common structural motifs widely displayed in agrochemicals, pharmaceuticals, and catalysts.[6] They have also been employed as highly useful building blocks in organic synthesis. Recently, the direct functionalization of alkenes triggered by *S*-[7] or *P*-centered[8] radical addition to alkenes has emerged as a prom-



Scheme 1 Hydrofunctionalization with diverse alkenols *via* 1,5(6)-HAT.

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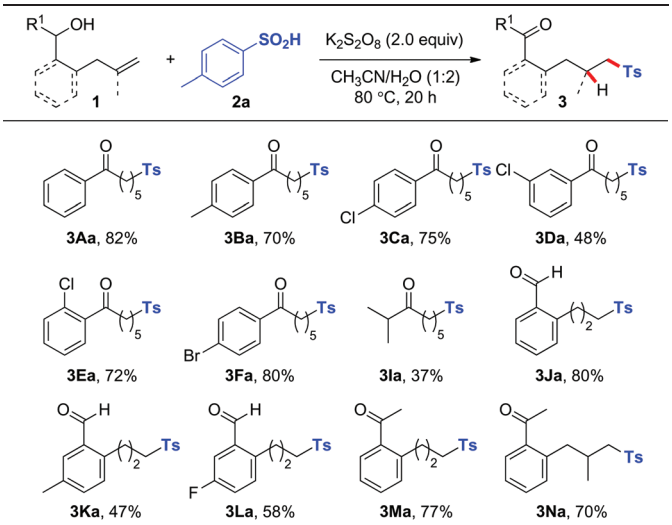
ising tool for the synthesis of functionalized organosulfones and organophosphorus compounds. Thus, much progress has been made in the development of sulfonylation and phosphonylation of activated olefins. However, the application of similar transformations to unactivated alkenes is more challenging,[9] which is probably due to the unfavorable reversible generation of unstable radical intermediates.[8a,10] As our continuing interest in the functionalization of unactivated alkenes *via* the addition of radicals to unactivated alkenes followed by subsequent remote functional group translocation,[11] we describe herein a general and efficient protocol for hydrosulfonylation, hydrophosphonylation, and hydroalkylation of alkenols in the presence or absence of a *gem*-disubstituent effect *via* intramolecular 1,5(6)-HAT in a highly controlled site-selective manner. It generally provides valuable sulfonyl-, phosphonyl-, and malonate-functionalized carbonyl compounds in good yields (Scheme 1b).

Results and discussion

At first, we began our investigation by exploring the hydrosulfonylation reaction of linear alkenol **1A** with *p*-toluenesulfinic acid **2a**. Various oxidants were investigated and only $K_2S_2O_8$ gave the desired product **3Aa** (entries 1–4, Table 1).[7e] An inert atmosphere was slightly beneficial for the reaction (entry 5). Three equiv. of **2a** together with two equiv. of $K_2S_2O_8$ were proven to be necessary for the full conversion of **1A** and the good yield of **3Aa** (entries 6–8). Switching the oxidant to $(NH_4)_2S_2O_8$ unexpectedly led to significantly diminished yield (entry 9). Co-solvent systems exhibited high reaction efficiency and resulted in a clear reaction mixture. Finally, we found that the reaction of **1A** with *p*-toluenesulfinic acid (**2a**) proceeded smoothly by simply using the cheap $K_2S_2O_8$ (2 equiv.) as the oxidant in CH_3CN/H_2O (1 : 2) at 80 °C for 16 h, providing sulfonylated ketone **3Aa** in 82% isolated yield.

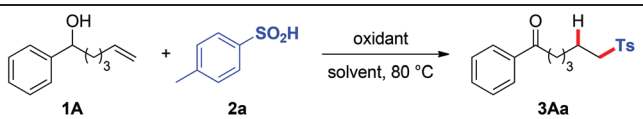
With the optimal reaction conditions in hand, we set out to explore the scope with respect to various alkenols (Table 2). A range of linear alkenols bearing diversely functionalized aryl groups (electron-rich one: Me for **1B**; electron-deficient ones: Cl for **1C–1E** and Br for **1F**) were found to be suitable substrates to give the corresponding products **3Ba–3Fa** selectively in 48–80% yields. It should be noted that substrate **1I**, with an isopropyl group in place of a phenyl one, also afforded the expected product **3Ia** albeit with lower yield, thus clearly demonstrating that the current process was not limited to benzylic alcohol. Comparable to linear alkenyl alcohols, the aryl-tethered substrates **1J–1N** were also applicable to this process, affording highly substituted Ts-containing aryl aldehydes **3Ja–3La** and aryl ketones **3Ma–3Na** in moderate to good yields. Notably, substrate **1N** with a *gem*-disubstituted alkenyl group reacted efficiently to afford aryl ketone **3Na** in 70% yield.

Table 2 Substrate scope of hydrosulfonylation[a,b]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.6 mmol), $K_2S_2O_8$ (0.4 mmol), CH_3CN (0.7 mL), H_2O (1.4 mL), 80 °C, 20 h. [b] Isolated yield.

Table 1 Reaction condition optimization for hydrosulfonylation[a]



Entry	Oxidant (*x* equiv.)	**2a** (*y* equiv.)	Solvent (ratio)	Yield[b] (%)
1	$Fe(NO_3)_3{\cdot}9H_2O$ (0.10), air	3.0	MeCN	Trace
2[c]	TBAI (0.10), TBHP (3.0)	3.0	Dioxane/H_2O (4/1)	Trace
3	Pyridine (4.0), air	5.0	DCE	NR
4	$K_2S_2O_8$ (1.0), air	3.0	MeCN/H_2O (1/2)	50%
5	$K_2S_2O_8$ (1.0), argon	3.0	MeCN/H_2O (1/2)	55%
6	$K_2S_2O_8$ (2.0), argon	1.0	MeCN/H_2O (1/2)	48%
7	$K_2S_2O_8$ (2.0), argon	2.0	MeCN/H_2O (1/2)	70%
8	**$K_2S_2O_8$ (2.0), argon**	**3.0**	**MeCN/H_2O (1/2)**	**82%[d]**
9	$(NH_4)_2S_2O_8$ (2.0), argon	3.0	MeCN/H_2O (1/2)	35%

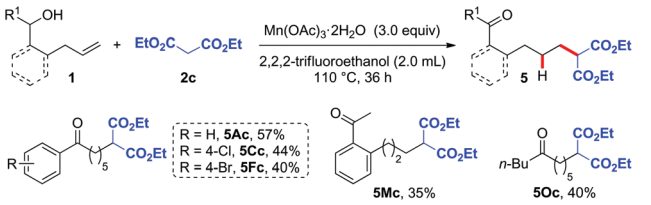
[a] Reaction conditions: **1A** (0.2 mmol), **2a**, solvent (2.0 mL) at 80 °C for 16 h under an argon atmosphere. [b] Determined by NMR spectroscopy using 1,3,5-trimethylbenzene as an internal standard. [c] *p*-Toluenesulfonylhydrazine was utilized. [d] Isolated yield.

Inspired by the above successful results, we next focused our attention on other challenging heteroatom- and carbon-centered radicals. A phosphonyl radical was then selected as the heteroatom-centered radical to probe whether a similar radical process could be realized.[8,9] After systematic optimization of different reaction parameters (Table S1†), we were delighted to find that in the presence of 3.0 equiv. of AgOAc[8i] or 50 mol% of $AgNO_3$,[8d] the reaction of alkenol substrates with 2.0 equiv. of $Ph_2P(O)H$ (**2b**) in DMF at 100 °C afforded the corresponding phosphonylated ketones in good yields (Table 3). The reaction tolerated a variety of linear alkenols containing aryl groups with different substituents to yield products **4Ab–4Cb** and **4Eb–4Hb** in 47–90% yields. Similarly, the aryl-tethered substrates **1J** and **1M** exhibited high efficiency in this hydrophosphonylation reaction. Good reactivity was also observed for the *gem*-disubstituted alkene substrate **1N** and aliphatic substrate **1O**, thus illustrating the wide applicability of the current hydrophosphonylation reaction.

In order to further expand the synthetic utility of this methodology, we next investigated the hydroalkylation of alkenols with *C*-centered radical precursors *via* the HAT strategy. Malonate, which is prone to undergoing oxidation to produce *C*-centered radicals, was then used to test our hypothesis.[12] After screening lots of reaction parameters (Table S2†), we optimized the reaction conditions of this hydroalkylation as follows: 3.0 equiv. of $Mn(OAc)_3$ as the oxidant and 2,2,2-trifluoroethanol as the solvent at 110 °C for 36 h.[12d] The reaction of various substrates **1A**, **1C**, **1F**, **1M**, and **1O** with malonate **2c** as the radical precursor gave the desired malonate-substituted ketone products **5Ac**, **5Cc**, **5Fc**, **5Mc**, and **5Oc** in moderate yields (Scheme 2).

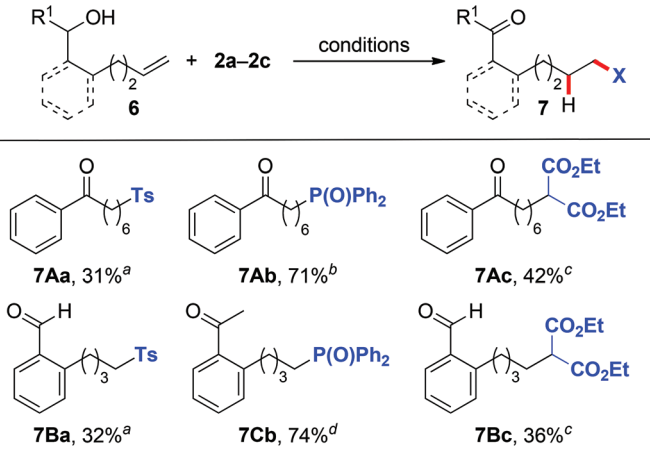
Inspired by the above success in the 1,5-HAT process, we subsequently switched our attention to the use of alkenols **6** with one-carbon-longer chains to probe whether the more challenging 1,6-HAT obtained *via* a higher energy seven-membered cyclic transition state[13] could be realized under the current reaction system. Gratifyingly, under the reaction conditions identical to those of the 1,5-HAT process (Tables 2, 3 and Scheme 2), remotely sulfonyl- (**7Aa**, **7Ba**), phosphonyl- (**7Ab**, **7Cb**), and malonate-substituted (**7Ac**, **7Bc**) aldehydes/ketones were obtained in moderate to good yields from alkenyl alcohols **6A–6C** (Table 4).

To gain insights into the reaction mechanism, several control experiments were performed. Firstly, the sulfonylation reaction was run under the standard conditions with the addition of radical scavengers such as benzoquinone (BQ) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The reactions were significantly inhibited by these reagents (Scheme 3, eqn (1)), indicating radical intermediates in the reaction. Secondly, the use of **[D$_1$]-1A** under the standard sulfonylation conditions led to the formation of **[D$_1$]-3Aa** with complete transposition of the α-D atom (Scheme 3, eqn (2)). Thirdly, no crossover products **3Aa** or **[D$_1$]-3Pa** were detected when equal molar amounts of **[D$_1$]-1A** and **1P** were used under the



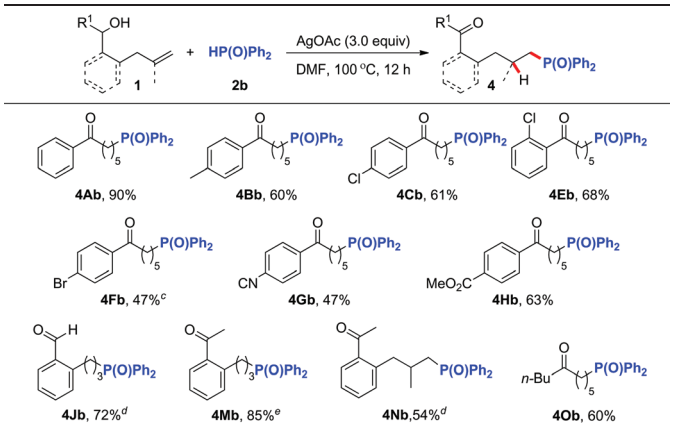
Scheme 2 Substrate scope of hydroalkylation. Reaction conditions: **1** (0.2 mmol), **2c** (0.3 mmol), $Mn(OAc)_3·2H_2O$ (0.6 mmol), 2,2,2-trifluoroethanol (2.0 mL), 110 °C, 36 h.

Table 4 Substrate scope of the 1,6-HAT process

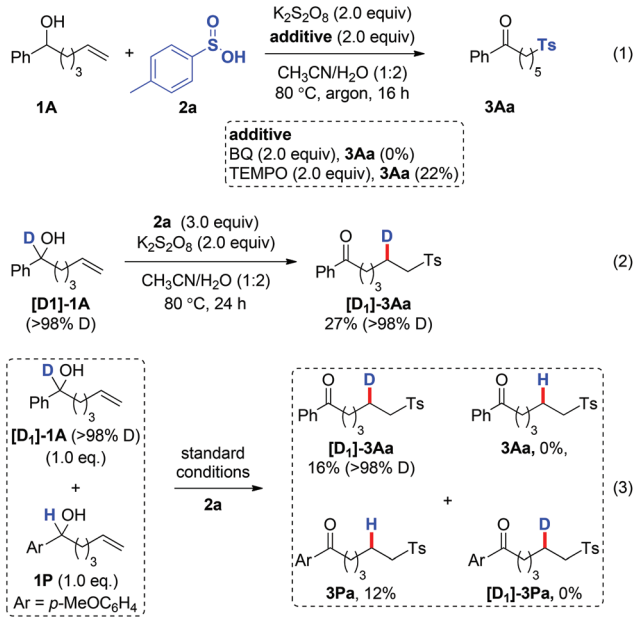


[a] Reaction conditions: **6** (0.2 mmol), **2a** (0.6 mmol), $K_2S_2O_8$ (0.4 mmol), CH_3CN (0.7 mL), H_2O (1.4 mL), 80 °C. [b] Reaction conditions: **6** (0.2 mmol), **2b** (0.4 mmol), AgOAc (0.6 mmol), DMF (2.0 mL), 100 °C. [c] Reaction conditions: **6** (0.2 mmol), **2c** (0.3 mmol), $Mn(OAc)_3·2H_2O$ (0.6 mmol), 2,2,2-trifluoroethanol (2.0 mL), 110 °C. [d] Reaction conditions: **6** (0.2 mmol), **2b** (0.4 mmol), $AgNO_3$ (0.6 mmol), DMF (2.0 mL), 100 °C.

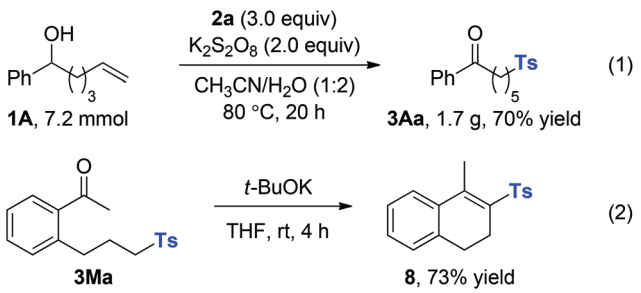
Table 3 Substrate scope of hydrophosphonylation[a,b]



[a] Reaction conditions: **1** (0.2 mmol), **2b** (0.4 mmol), AgOAc (0.6 mmol), DMF (2.0 mL), 100 °C, 12 h. [b] Isolated yield. [c] Forty percent of the starting material was recovered. [d] $AgNO_3$ (0.6 mmol) was used instead of AgOAc. [e] $AgNO_3$ (0.1 mmol) was used instead of AgOAc.



Scheme 3 Control experiments.



Scheme 4 Large scale preparation and transformation.

standard conditions, which excludes an intermolecular HAT process (Scheme 3, eqn (3)).

To illustrate the potential synthetic applicability of this protocol, **3Aa** was prepared in large scale to indicate that no significant erosion in the reaction efficiency had occurred (Scheme 4, eqn (1)). The utility of our protocol was further demonstrated by cyclization of the obtained ketone **3Ma** under basic conditions at room temperature to afford the α,β-unsaturated sulfone product **8** in 73% yield; **8** is a good Michael acceptor widely applied in biotransformation and organic synthesis (Scheme 4, eqn (2)).

Conclusions

In summary, we have successfully developed a general and efficient radical protocol for the concomitant diverse hydrofunctionalization of alkenes and oxidation of remote alcohols. It provides valuable sulfonyl-, phosphonyl-, and malonate-substituted ketones or aldehydes through ketyl radical intermediates *via* 1,5(6)-HAT triggered by addition of the corresponding *S*-, *P*-, and *C*-centered radicals to alkenes in an *anti*-Markovnikov manner. This mild and versatile method exhibits a broad substrate scope in regard to alkenols with or without *gem*-disubstituted tethering groups and tolerates a series of carbon- and heteroatom-centered radical precursors.

Experimental

General procedure for the radical hydrosulfonylation reaction system

To a flame-dried Schlenk tube equipped with a magnetic stir bar were added **1** (0.2 mmol), **2a** (0.6 mmol), and $K_2S_2O_8$ (0.4 mmol). The tube was evacuated and backfilled with argon three times, and then MeCN (0.7 mL) and H_2O (1.4 mL) were added. The tube was stirred at 80 °C for 18 h and then H_2O (5 mL) was added. EtOAc was used to extract the product from the aqueous layer (3 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified using flash column chromatography to afford the product **3**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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