Heterocycle Synthesis

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Radical-Mediated 1,2-Formyl/Carbonyl Functionalization of Alkenes and Application to the Construction of Medium-Sized Rings

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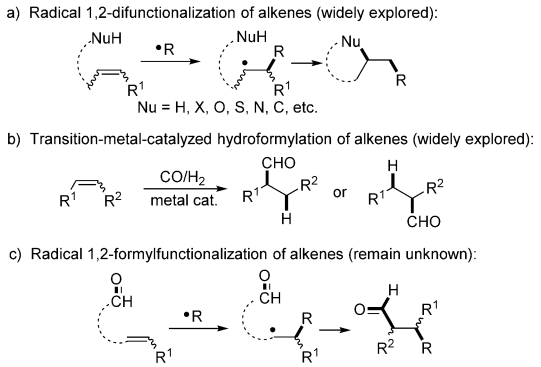
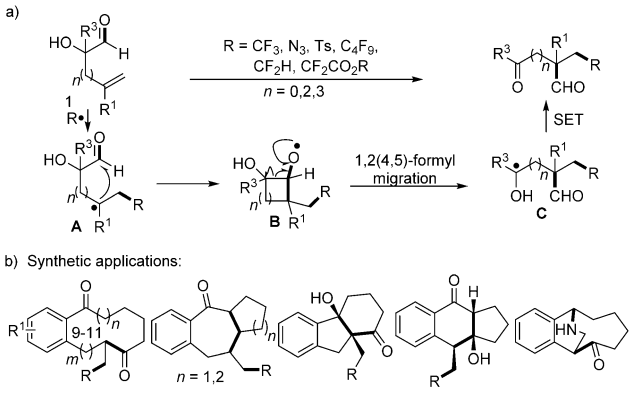
Abstract: *A novel radical 1,2-formylfunctionalization of alkenes involving 1,2(4,5)-formyl migration triggered by addition of various carbon- and heteroatom-centered radicals to alkenes has been developed for the first time, thus providing straightforward access to diverse β-functionalized aldehydes with good efficiency, remarkable selectivity, and excellent functional group tolerance. Analogous transformations mediated by a keto-carbonyl migration have also been effected under similar conditions. This method was used to access ring systems including various benzannulated nine-, ten-, and eleven-membered rings, complex 6-5(6,7)-6(5) fused rings, and bridged rings with diverse functionalities.*

Given the intensified research efforts over the past three decades, the 1,2-functionalization of alkenes has evolved into an efficient tool for the preparation of complex organic molecules.[1] In particular, radical-mediated direct olefinic 1,2-functionalization initiated by intermolecular addition of both carbon- and heteroatom-centered radicals to alkenes has emerged as one of the most attractive strategies for the simultaneous formation of two vicinal chemical bonds involving halo-, oxy-, thio-, amino-, and carbo-functionalization, by using a variety of radical precursors and trapping reagents (Scheme 1a).[2] Despite these impressive advances, 1,2-difunctionalization-type radical formylation reaction of alkenes, involving the concurrent incorporation of a formyl group and a radical species, to our knowledge, still remains a formidable and unexplored challenge, largely because of the unavailability of appropriate formyl trapping reagents (Scheme 1c).[3] Given that the resultant β-functionalized aldehydes are valuable final products and intermediates in the synthesis of bulk chemicals like alcohols, esters, and amines, the formylation of simple alkenes should be of great importance in both academia and industry. One outstanding example is the transition-metal-catalyzed hydroformylation by the addition of CO and H_2 to an alkene, a reaction which is one of the largest industrially applied processes (Scheme 1b).[4] In this process, only one new carbon–carbon bond is formed, while the 1,2-difunctionalization-type formylation reaction of alkenes for generating β-functionalized aldehydes with concomitant incorporation of diversely functional groups in one step remains a challenge (Scheme 1c).



Scheme 1. 1,2-Difunctionalization of alkenes.

In this context and as part of our continuous efforts in radical-initiated remote migration chemistry,[5] we became interested in developing a novel radical difunctionalization-type scenario to address the above challenge (Scheme 2a). In this scenario, we envisioned that various in situ generated radicals might selectively add to the alkene bonds of the rationally designed substrates **1**, thus producing a transient alkyl radical intermediate (**A**).[2] Driven by the formation of a lower-energy neutral ketyl radical **C**,[6] **A** would preferentially undergo a radical cyclization to form the alkoxy radical **B**[7] with subsequent selective β-fragmentation[8] to realize 1,2-formylfunctionalization of alkenes. To realize this scenario, several major challenges need to be overcome: 1) the high



Scheme 2. 1,2-Formylfunctionalization of alkenes and synthetic applications. TsCl = 4-toluenesulfonyl chloride.

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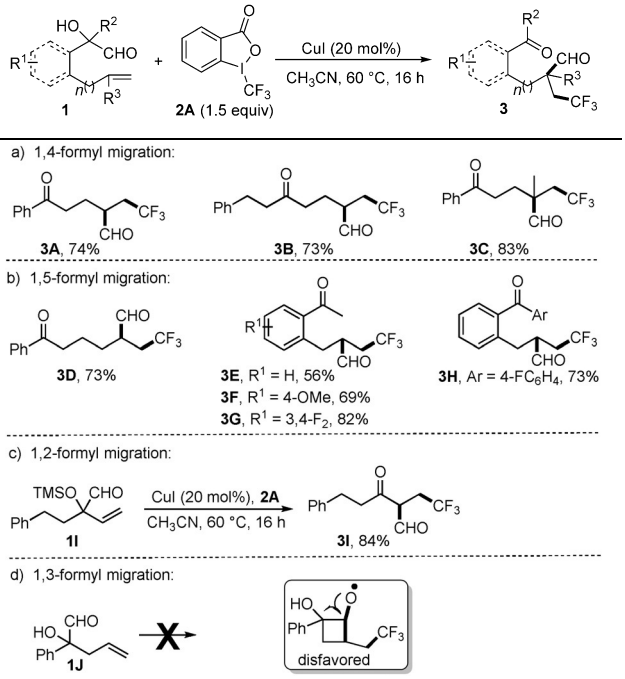
tendency of **B** toward hydrogen abstraction for the formation of undesired cyclic alcohols;[7,8] 2) selective control of promiscuous reactivity, such as the competitive 1,2-difunctionalization of alkenes with oxygen-based nucleophiles, β-hydride elimination, and other transformations of **A** with multiple reactive sites;[2,9] 3) the identification of appropriate oxidative conditions for the generation of the radical species while suppressing the oxidation of the sensitive aldehyde group. Herein we report the successful development of the first radical olefinic 1,2-difunctionalization-type formylation by either a 1,2-, 1,4-, or 1,5-formyl radical migration triggered by either trifluoromethylation, azidation, sulfonylation, perfluoroalkylation, or difluoromethylation of unactivated alkenes to afford diversely β-functionalized aldehydes (Scheme 2a). Most importantly, this strategy could also provide convenient access to various benzannulated nine-, ten-, and eleven-membered rings for further transformation into different types of ring systems including complex 6-5(6,7)-6(5) fused rings and bridged rings with diverse functionalities (Scheme 2b). Such medium-sized motifs are challenging synthetic targets, mainly because of the unfavorable enthalpic and entropic parameters for the conventional cyclization-based methods.[10]

The increasing importance of trifluoromethylated organic molecules for the synthesis of pharmaceuticals and agriculture chemicals has spurred vigorous research for the exploration of more powerful and practical trifluoromethylation protocols.[11] To this end, we initiated these investigations by examining the reaction of 2-hydroxy-2-phenylhex-5-enal (**1A**) with the commercially available Togni's reagent[12] (**2A**). To our delight, the 1,2-trifluoromethylformylation reaction proceeded smoothly in the presence of CuI (20 mol%) with EtOAc as the solvent at 80°C for 16 hours, thus giving the desired β-trifluoromethylated aldehyde **3A** (for structure see Table 1) in 64% yield and clearly demonstrated that the remote radical 1,4-formyl migration was much more favorable than other reaction pathways in the current catalytic system (see Table S1, entry 1 in the Supporting Information). Upon screening the reaction conditions, we identified the following protocol as optimal: the reaction of **1A** and **2A** with a molar ratio of 1.0:1.5 in the presence of CuI (20 mol%) in CH_3CN at 60°C for 16 hours (Table S1, entry 7). With the optimal reaction conditions established, the generality of the current catalytic system for the 1,2-trifluoromethylformylation of alkenes by radical 1,4-formyl migration was next investigated and the results are summarized in Table 1. Different linear alkenyl α-hydroxyaldehydes reacted to give the products **3A** and **3B** selectively in 74 and 73% yields, respectively. Moreover, the substrate **1C**, with a geminal-disubstituted alkenyl group, was also well tolerated and gave **3C** containing an α-quaternary carbon center in 83% yield. We then switched our synthetic target to test the 1,5-formyl migration process. Gratifyingly, under reaction conditions identical to those of the 1,4-formyl migration process, the reaction of the linear substrate **1D** proceeded smoothly to generate **3D** in 73% yield. The aryl-tethered substrates bearing electron-neutral (**1E**), electron-rich (**1F**), and electron-deficient (**1G**) aryl groups proved to be suitable substrates, thus furnishing the corresponding products **3E**–**3G** in

Table 1: Scope of the 1,2-trifluoromethylformylation reaction.[a,b]

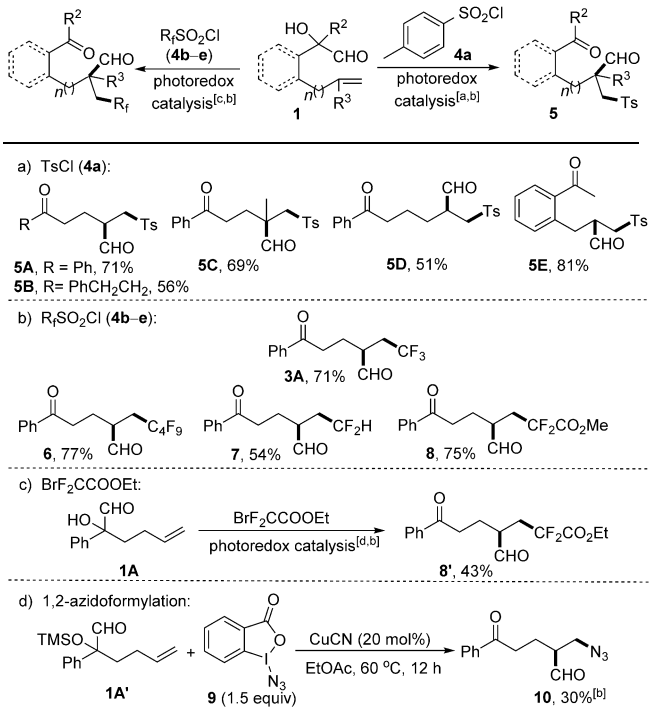


[a] All of the reactions were conducted on a 0.20 mmol scale. [b] Yields of isolated products based on **1**.

56–82% yields. The substrate **1H**, having an aryl ring α to the alcohol group, reacted efficiently to afford **3H** in 73% yield. We also found that the desired product **3I**, from a 1,2-formyl radical migration triggered by trifluoromethylation of alkene, was obtained in 84% yield in the case of the TMS-protected α-hydroxy substrate **1I** (Table 1c). However, treatment of the substrate **1J** under otherwise identical reaction conditions hardly generated any desired product expected from the 1,3-formyl migration, thus indicating that the migration transition state, a four-membered ring, might be disfavored for generating **1J** (Table 1d).

The scope of the reaction was further expanded to other radical precursors. Unfortunately, our initial attempts to use either *p*-toluenesulfinic acid or *p*-toluenesulfonyl hydrazide in the presence of different oxidants as a way to generate the sulfonyl radicals in situ for the reaction failed (see Table S2), presumably because of the incompatibility of strong oxidants with the sensitive formyl group under these reaction conditions. In recent years, visible-light-driven photoredox catalysis has become an ecofriendly and powerful tool for the generation of various radical species under extremely mild reaction conditions without the need for external oxidants.[13] Therefore, we surmised that the use of photoredox catalysis may be suitable for the development of olefinic 1,2-sulfonylformylation. As expected, the reaction of **1A** with *p*-toluenesulfonyl chloride (**4a**) in the presence of $[Ir(ppy)_2(dtbbpy)]PF_6$ (1 mol%) with 2 equivalents of Na_2HPO_4 under visible light delivered the β-sulfonyl aldehyde **5A** in 71% yield (Table 2a) after a systematic optimization of different reaction parameters (see Table S2).[14] Similar results were obtained in the reaction of a series of alkenyl

Table 2: Scope of other radical-mediated 1,2-formyl functionalizations.

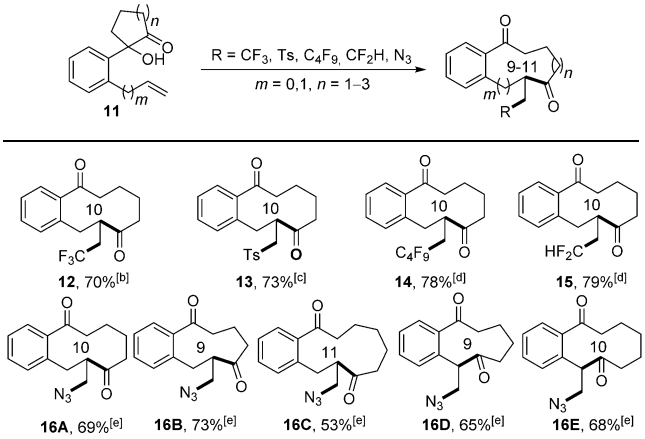


[a] Reaction conditions: **1** (0.20 mmol), TsCl (1.5 equiv), $[Ir(ppy)_2(dtbbpy)]PF_6$ (1 mol%), Na_2HPO_4 (2.0 equiv), EtOAc (2 mL), blue LED at RT for 5 h under argon. [b] Yield of the isolated product based on **1**. [c] Reaction conditions: **1** (0.20 mmol), R_fSO_2Cl (1.5 equiv), $[Ir(ppy)_2(dtbbpy)]PF_6$ (1 mol%), Na_2HPO_4 (2.0 equiv), EtOAc (2 mL), blue LED at RT for 5 h under argon. [d] Reaction conditions: **1** (0.20 mmol), BrF_2CCO_2Et (2.0 equiv), $[Ir(ppy)_2(dtbbpy)]PF_6$ (1 mol%), Na_2HPO_4 (2.0 equiv), CH_2Cl_2 (2 mL), blue LED at RT for 5 h under argon. dtbbpy = di-*tert*-butylbipyridine, ppy = phenylpyridyl, TMS = trimethylsilyl.

α-hydroxyaldehydes to afford the expected products **5B**–**E** in 51–81% yields (Table 2a). Most importantly, all radicals generated in situ from trifluoromethyl-, perfluorobutyl-, difluoromethyl-, and difluoroacetyl-sulfonyl chloride (**4b**–**e**)[15] by extrusion of sulfur dioxide under similar reaction conditions were found to be applicable to generate **3A**, and **6**–**8** in 54–77% yields (Table 2b). Since $BrCF_2CO_2Me$ is commercially available and has also been utilized in photoredox catalysis,[16] this reagent was also successfully applied for this strategy to produce the desired product **8′** in 43% yield (Table 2c). To expand the synthetic utility of this methodology, we next focused our attention on the azide radical generated from the iodine(III) reagent azidoiodinane **9** reported by Zhdankin and co-workers.[17] However, treatment of **1A** with **9** in the presence of different copper catalysts afforded almost no desired product. Subsequently, we chose the TMS-protected α-hydroxy substrate **1A′** as the substrate and found that the expected 1,2-azidoformylation reaction could be realized to afford the β-azido aldehyde **10**, albeit with 30% yield, in the presence of CuCN (20 mol%) at 60 °C in EtOAc for 12 hours (Table 2d).

Medium-ring structures constitute basic skeletons of many important naturally occurring and biologically active molecules. The development of general strategies for the construction of such backbones has been a longstanding and challenging topic in organic synthesis.[10] In view of this, we rationally designed the alkenyl cyclic α-hydroxyketones **11** (Table 3), in which the selective addition of diverse radicals to

Table 3: Construction of medium-sized molecules by carbonyl migration.[a]



[a] Yield of isolated product based on **11**. [b] Reaction conditions are similar to those of **3** except EtOAc is used as a solvent. [c, d, e] Reaction conditions similar to those for **5**, **6**, **7**, and **10**.

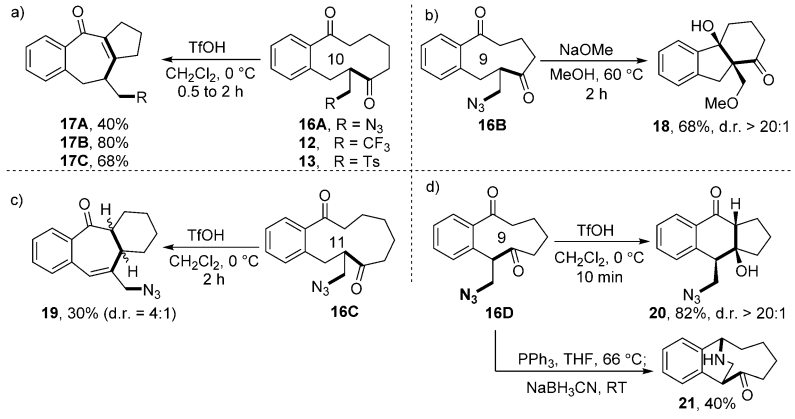
the alkene moieties could trigger ring expansion by a similar remote 1,4- or 1,5-carbonyl migration process. To our delight, the allylbenzene derivative **11A** formed the expected product **12** in 70% yield under the reaction conditions almost identical to those of 1,2-trifluoromethylformylation reaction. Furthermore, the generated sulfonyl, perfluorobutanyl, difluoromethyl and azide radicals were well-tolerated to provide **13**–**16A** in 69–79% yields. To increase the diversity of such strategy, the azido-substituted nine- and eleven-membered dicarbonyl products **16B** and **16C** were also obtained in 73 and 53% yields, respectively, from the corresponding substrates. Additionally, the styrene derivatives were also suitable substrates for such a process to provide nine- and ten-membered rings **16D** and **16E** in 65 and 68% yields, respectively. Notably, the obtained benzannulated medium-sized rings are the core structures of many biologically active natural products such as clavilactone A and cytochalasin G.[18]

An important synthetic application is that the radical functionalized medium-sized diketones can serve as a convenient handle to access other useful motifs by further manipulation. For example, treatment of the 1,6-dicarbonyl products **16A**, **12**, and **13** with trifluoromethanesulfonic acid (TfOH) provided the 6-7-5 fused rings **17A**–**C** in 40–80% yields (Scheme 3a). In addition, treatment of **16B** with NaOMe generated the 6-5-6 fused ring **18** in 68% yield with excellent diastereoselectivity (>20:1 d.r.), wherein the azido group was simultaneously replaced by a methoxy group, thus suggesting its role as a leaving group (Scheme 3b). Similarly, in the presence of TfOH, **16C** and **16D** afforded the 6-7-6 fused ring **19** (30% yield with 4:1 d.r.) and 6-6-5 fused ring **20** (82% yield with >20:1 d.r.), respectively (Scheme

3c,d). To further exemplify the synthetic importance of azido group in the product, the PPh_3-promoted intramolecular Staudinger/aza-Wittig reaction of **16D**, followed by selective reduction with sodium cyanoborohydride ($NaBH_3CN$) generated the bridged amine **21** in 40% yield (Scheme 3d). It should be noted that the fused 6-5(6,7)-6(5) tricyclic ring and bridged ring systems are privileged structural motifs found in natural products and pharmaceutical compounds, such as sodium channel grayanotoxins, the antibacterial and antitumor icetexane family, and a benzindene prostaglandin analogue.[19]

To obtain some insight into the reaction mechanism, radical-trapping experiments were conducted by employing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 1,4-benzoquinone (BQ). The reaction of **1A** and **2A** was found to be inhibited by these reagents, thus suggesting that the reaction is a radical-based process (see Scheme S1). In addition, the preliminary kinetic studies (see Figures S1a–c and S2a,b) show that the reaction is zero-order in **1A** and second-order with respect to **2A**. It is quite possible that **1A** was not involved in the rate-determining step and that the reaction process has two rate-determining steps, both of which involve **2A**. However, the exact mechanism remains unclear at present and deserves further detailed study.

In summary, we have successfully developed the first radical 1,2-difunctionalization-type formylation of alkenes by 1,2-, 1,4-, and 1,5-formyl radical migration triggered by trifluoromethylation, azidation, sulfonylation, perfluoroalkylation, and difluoromethylation of unactivated alkenes. This method offers a novel and sustainable radical reaction to deliver diverse β-functionalized aldehydes with good efficiency, remarkable selectivity, and excellent functional-group tolerance. More significantly, this method can be applied for the keto-carbonyl migration, thus constructing synthetically challenging benzannulated medium-sized ring scaffolds, which can be easily transformed into a series of very useful complex 6-5(6,7)-6(5) fused and bridged ring systems, thus demonstrating the high synthetic utility of the current process in organic and medicinal chemistry.



Scheme 3. Versatile transformations. THF = tetrahydrofuran, TfOH = trifluoromethanesulfonic acid.

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