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Authors: Zhuangzhi Shi

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Radical Addition Enables 1,2-Aryl Migration from Vinyl-Substituted All-Carbon Quaternary Center

Zexian Li, Minyan Wang, and Zhuangzhi Shi*

Dedicated to the 100th anniversary of the School of Chemistry and Chemical Engineering, Nanjing University

Abstract: An efficient method for photocatalytic perfluoroalkylation of vinyl-substituted all-carbon quaternary centers involving 1,2-aryl migration has been developed. The rearrangement reactions use fac-Ir(ppy)3, visible light and commercially available fluoroalkyl valuable halides and can generate multisubstituted perfluoroalkylated compounds in a single step that would be challenging to prepare by other methods. Mechanistically, the photoinduced alkyl radical addition to an alkene leads to the migration of a vicinal aryl substituent from its adjacent all-carbon quaternary center with the concomitant generation of C-radical bearing two electron-withdrawing groups that is further reduced by a hydrogen donor to complete the domino sequence.

Rearrangement reactions are among the most attractive transformations in the field of chemical synthesis, and these reactions are convenient, efficient and atom-economic procedures for constructing organic compounds with new skeletons.^[1] Among these reactions, radical-mediated functionality migration has gained increasing attention.^[2] Radical-induced 1,2-rearrangement is the subject of considerable interest in this area.^[3] The first radical 1,2migration in β -aryl carbon-centered radicals, named the neophyl rearrangement, was discovered by Urry and Kharasch in 1944.^[4] However, the limited substrate scope, slow process and harsh reaction conditions make it difficult to apply in organic synthesis.

During the last decade, some well-designed olefins have been developed by many research groups for radical-induced 1,2-rearrangement. For example, the semipinacol-type rearrangement^[5] of allylic alcohols has been explored for the preparation of diverse β -functionalized ketones (Figure 1a).^[6] Furthermore, the 1,2-metalate rearrangement^[7] of vinylboronate complexes has been uncovered by using Et₃B/air,^[8] visible light^[9] or nickel catalysts^[10] (Figure 1b). Inspired by these results, our group also developed a photoredox olefinic 1,2-boryl-migration by radical addition to build gem-bis(boryl)alkanes.^[11] In addition, the Studer group has recently disclosed a novel 1,2-boryl-migration using allylboronic esters to access radical 1,3-difunctionalization products (Figure 1c).^[12] Herein, we first describe that a class of

a) Semipinacol-type rearrangement of allylic alcohols:







Figure 1. Radical-induced 1,2-migration in olefins.

olefins bearing adjacent all-carbon quaternary centers can undergo 1,2-aryl migration through radical addition (Figure 1d).

The installation of a perfluoroalkyl substitution into organic compounds typically results in great changes in their properties like the polarity, solubility, conformational behavior, and metabolic stability.^[13] Perfluoroalkylation of alkenes has been one of the most efficient methods for introducing perfluoroalkyl substitution into organic molecules.^[14] Different from the reported process, this reaction proceeds through perfluoroalkyl-radical addition to the olefinic double bonds, and the adduct radical undergoes 1,2-aryl migration to afford a translocated C-radical, which is further reduced by a hydrogen donor.^[15] Visible-light photoredox catalysis^[16] makes this strategy possible under mild reaction conditions, resulting in a new synthetic method for valuable multi-substituted perfluoroalkylated compounds.

We started the investigations by treatment of olefin **1a** with I-^{*n*}C4F₉ (**2a**) (Table 1). The rearrangement was found to be facile with 1.0 mol% *fac*-[Ir(ppy)₃] as the photocatalyst (PC), 2.0 equiv of DBU as the base, in the presence of an additive, TMDEA (2.0 equiv) in TFE after 12 h at room temperature under irradiation with blue LEDs, and the desired product **3aa** was produced in 78% yield (entry 1). Under these reaction conditions, a byproduct **4aa** derived from atom transfer radical addition (ATRA)^[17] was formed in trace amounts. Replacing the PC with [Ru(bpy)₃]Cl₂ or [Ir(ppy)₂(dtbby)]PF₆ afforded a mixture of **3aa** and **4aa** (entries 2-3). Significantly, DBU and

^[*] Z. Li, Assoc. Prof. Dr. M. Wang, and Prof. Dr. Z. Shi State Key Laboratory of Coordination Chemistry, Chemistry and Biomedicine Innovation Center (ChemBIC), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093 (China) E-mail: shiz@nju.edu.cn

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Table 1. Reaction development.[a]

	1.0 mol% [fac-lr(ppy) ₃] ■ DBU/TMEDA ■ TFE, Ar, rt, 12h	EtOOC Ph	^r C₄F _{9 +} Ph∖ FtOOC	
1a	Blue LEDs I- ⁿ C ₄ F ₉ (2a)	3aa	2,000	4aa
Entry	Variation from the standard conditions		Yield of 3aa (%) ^[b]	Yield of 4aa (%) ^[b]
1	None		78 (73) ^[c]	<10
2	Using [Ru(bpy) ₃]Cl ₂ as PC		15	44
3	Using [Ir(ppy) ₂ (dtbby)]PF ₆ as PC		27	23
4	Without DBU		39	34
5	Without TMEDA		<10	44
6	Using NEt ₃ instead of DBU		33	<10
7	Using quinuclidine instead of DBU		25	<10
8	Using MeOH instead of TFE		41	0
9	Using HFIP instead of TFE		55	0
10	Using DCM instead of TFE		28	8
11	Without [fac-Ir(ppy) ₃]		8	57
12	In the dark		0	0

^[a]Reaction conditions: 1 mol% PC, **1a** (0.20 mmol), **2a** (0.40 mmol), DBU (0.40 mmol), TMEDA (0.40 mmol) in TFE (1.0 mL), blue LEDs, at room temperature under Ar for 12 h. ^[b]GC yield. ^[c]Isolated yield after chromatography. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; TMEDA = N,N,N,N'-tetramethylethylenediamine.

TMEDA could accelerate the rearrangement process (entries 4-5). Other organic bases, such as NEt₃ and quinuclidine, exhibited much lower reactivity for this transformation (entries 6-7). The TFE was superior to other alcohol solvents, such as MeOH and HFIP (entries 8-9). When the reaction was conducted in non-protonic solvents, such as DCM, the desired product **3aa** could also generate, albeit with a much lower conversion (entry 10). Finally, control experiments showed that both the PC and visible light were required for the rearrangement (entries 11-12). The ATRA product **4aa** could be formed in the absence of PC in accordance with a radical chain propagation process.

With the optimized reaction conditions in hand, we first performed a series of experiments to examine the scope of the alkyl halides in this rearrangement reaction (Table 2). These mild redox conditions were compatible with perfluoroalkyl iodides bearing longer chains, such as ${}^{n}C_{6}F_{13}I$ (2b) and ${}^{n}C_{8}F_{17}I$ (2c). Difluoromethylating alkyl bromides 2d-e were also suitable substrates, and a monofluoromethylating substrate 2f provides the corresponding product 3af with poor diastereoselectivity. The generality of this reaction was further proved by successful expansion to 1,1,1-trifluoro-2-iodoethane (2g) and analogs 2h-2i with longer perfluorinated chains. Furthermore, tertiary aliphatic perfluoroalkyl iodides 2j-2k could also be employed as radical precursors. Notably, the reaction is not limited to the fluoro-containing substrates. Other alkyl halides, such as ethyl 2-iodoacetate (21), and 2iodoacetonitrile (2m), could also be used for the reaction, affording desired products 2al-2am in good yields.

Given the important function of the fluoromethyl groups,^[18] we further anticipated that the 1,2-aryl migration would be triggered by fluoromethylation (Scheme 1). When an

Table 2. Substrate scope of alkyl halides.^[a]



^[a]Reaction conditions: 1.0 mol% *fac*-[Ir(ppy)₃], **1a** (0.20 mmol), **2** (0.40 mmol), 2.0 equiv of DBU, 2.0 equiv of TMEDA, in 1.0 mL TFE irradiated by blue LEDs, at room temperature under Ar for 12 h; Isolated yield. ^[b] Irradiated by 40 W blue LED.

inexpensive and abundant agent CF₃I (**2n**) was submitted to the reaction conditions with olefin **1a**, the desired product **3an** was generated in 69% yield. Gratifyingly, a higher yield of **6** (75%) was observed while the reaction was performed using a TMEDA·2CF₃I adduct **2n'**.^[19] Furthermore, difluoromethylation of olefin **1a** with difluoromethyl 2-pyridyl sulfone **2o** (Hu's reagent)^[20a] was also facile to provide the rearrangement product **3ao** in 56% yield. Efforts to realize the monofluoromethylation of olefin proved challenging, and the use of fluorosulfoximine reagent **2p**^[20b] only showed low reactivity, potentially owing to the lack of radical stabilizing groups.



Scheme 1. Fluoromethylation/1,2-aryl migration of alkene 1a.

A broad range of olefins can participate in this rearrangement reaction with perfluoroalkyl iodide 2a as well

(Table 3). Aryl motif bearing electron-donating and electrondeficient substituents including OMe (1b), phenyl (1c), F (1d), Br (1e) and CN (1f) groups at the para position facilitated facile migration, leading to products 3ba-3fa in 54-89% yields. Substituents, such as CF₃ (1g), COOEt (1h) and Cl (1i) in the meta position of the aryl substituents were also compatible. Product 3ja resulted from the migration of a naphthyl group was isolated in moderate yield. Moreover, heteroaryl substrate 1k was submitted to the system and was found to give rearrangement product 3ka in 80% yield. Pleasingly, this strategy allowing for the rearrangement of olefins contains diverse EWGs. The analogue 11 with two COOMe substituents was readily transformed into 3la in a modest yield. The olefin 1m bearing one cyano and one ester group was also compatible. However, reaction of substrate 1n possessing a bulky barbituric acid motif with perfluoroalkyl iodide 2a provided ATRA product 4na as a major product with trace amounts of the desired product **3na** (<10%). Notably, in the case of using Hu's reagent 20 with olefin 1n, the absence of I atom in substrate resulted in a much higher conversion for the rearrangement product, leading to the compound **3no** in 51% yield. In addition, the rearrangement of ethyl 2-ethyl-2-phenylbut-3-enoate (10) containing only one EWG became very sluggish, in which the ATRA compound 40a was detected as a major product as well (not shown in the Table).

Table 3. Substrate scope of olefins.^[a]



^[a]Reaction conditions: 1.0 mol% *fac*-[Ir(ppy)₃], **1** (0.20 mmol), **2a** (0.40 mmol), 2.0 equiv of DBU, 2.0 equiv of TMEDA, in 1.0 mL TFE irradiated by blue LEDs, at room temperature under Ar for 12 h; Isolated yield. ^[b]**2o** (0.40 mmol), without DBU, 4.0 equiv of TMEDA, 24 h.

Because the rearrangement products contain two EWGs, we next carried out some downstream transformations to demonstrate the versatility of the current method (Scheme 2). The trifluoromethylation reaction can be scalable to a 2.0 mmol scale to afford compound **3an** in 58% yield. This compound could

selectively be reduced to diol **5** (89%) or undergo decarboxylation to ester **6** (81%) in good yields. Products bearing new all-carbon quaternary centers could be generated from Michael addition (**7**), nucleophilic substitution (**8-9**) and Aldol reaction (**10**) in 73-84% yields. Finally, bromination of product **3an** with NBS in the presence of a base produced compound **11** in a modest yield.



Scheme 2. Follow-up transformations of compound 3an.

Some experiments were also performed to gain insight into the potential mechanism of this rearrangement (Scheme 3). Treatment of byproduct **4aa** in the reaction did not form product **3aa**, excluding **4aa** as the possible intermediate in this reaction (Scheme 3a). As reported by Sodeoka's results,^[21] the reaction of compounds **12-13** with longer alkenyl chains formed cyclized products **14** and **15**, and 1,n-aryl migration products were not detected (Scheme 3b). When the reaction of olefin **1a** and alkyl halide **2d** was conducted with d1-MeOH as the solvent, D labeling was nearly fully incorporated into **3aa**. Further detected by ¹³C NMR, the reaction mixture generated two signals at 90.4 and 54.8 ppm, consistent with the formation of d1-methoxymethanol (**16**) in this reaction.^[22] Moreover, treatment of compound **3aa** in d1-MeOH did not form deuterium product D-**3aa** (Scheme 3c). These results illustrate



Scheme 3. Mechanistic experiments.

that the H/D exchange process occurs during the reaction, and the alcohol solvent acts as a donor of the hydrogen atom for the products. Furthermore, "light/dark" experiments further confirmed that visible light was a necessary component of the reaction. In addition, quantum yield measurements of the reaction between olefin **1a** with I-^{*n*}C4F9 (**2a**) yielded a value of $\Phi = 1.8$ (see Supporting Information).^[23] This result indicates that productive short-lived radical chain propagation processes perform alongside the main photoredox cycle.^[24]

Based upon the above results and the previous reports, a possible mechanism has been suggested in Figure 2. Photoexcitation of the $\ensuremath{Ir^{III}}$ complex with visible light affords a redox-active excited state *Ir^{III} that undergoes single electron transfer (SET) with alkyl halides 2 to produce an Ir^{IV} species and an alkyl radical I. The formed Ir^{IV} complex undergoes SET with tertiary amines to recover the IrIII species and generate an amine radical cation A.^[25] Then, species A can engage in hydrogen atom transfer with the TFE solvent, delivering an aminium species **B** and carbon-centered radical **C**. Further β -H elimination delivers CF₃CHO and a hydrogen atom radical. We observed the formation of trifluoroethoxy hemiacetal 17 by NMR from the reaction mixture, which was assumed to be formed from CF₃CHO and TFE.^[26] Similarly, the use of d1-MeOH as the solvent generates the deuterium product D-3aa and HCHO, which can further react with d1-MeOH resulting in compound 20 according to the experimental results. In addition, the formed radical I undergoes addition to olefin 1, providing an alkyl radical II. Sequential 1,2-aryl migration via spiro[2.5]octadienyl radical transition state III results in the formation of a radical IV. Finally, the resulting radical IV abstracts the formed hydrogen to yield the desired product 3. Out of the catalytic cycle, the alkyl radical II can participate in a propagation chain process with alkyl halides 2 to form ATRA product 4.



Figure 2. Plausible mechanism.

In summary, we have developed a general method for the efficient and divergent assembly of multisubstituted

perfluoroalkylated organic compounds by visible-light photoredox catalysis. This strategy uses a series of vinylsubstituted all-carbon quaternary centers to access cascade radical addition, rearrangement, and reduction processes, enabling one C-C bond cleavage along with one C-H and two C-C bond formations simultaneously. Further studies expanding upon the scope of this rearrangement as well as further mechanistic investigations are currently underway.

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Rearrangement · fluorine · photochemistry · radicals · olefins

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Rearrangement

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Radical Addition Enables 1,2-Aryl Migration from Vinyl-Substituted All-Carbon Quaternary Center



Lighting up: A photocatalytic system was developed for perfluoroalkylation of vinylsubstituted all-carbon quaternary centers using perfluoroalkyl halides with concomitant 1,2-aryl migration. This strategy possesses good functional group compatibility and can serve as a powerful synthetic tool for construction of valuable perfluoroalkylated compounds that would be difficult to prepare by other methods.