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Silver-Catalyzed Radical Phosphonofluorination of Unactivated Alkenes

Chengwei Zhang, Zhaodong Li, Lin Zhu, Limei Yu, Zhentao Wang, and Chaozhong Li*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P.R. China

Supporting Information

ABSTRACT: We report herein a mild and catalytic phosphonofluorination of unactivated alkenes. With catalysis by $AgNO_3$, the condensation of various unactivated alkenes with diethyl phosphite and Selectfluor reagent in CH_2Cl_2/H_2O/HOAc at 40 °C led to the efficient synthesis of β-fluorinated alkylphosphonates with good stereoselectivity and wide functional group compatibility. A mechanism involving silver-catalyzed oxidative generation of phosphonyl radicals and silver-assisted fluorine atom transfer is proposed.

The increasing importance of fluorine in agrochemicals and pharmaceuticals[1] as well as the use of ^{18}F-labeled organic compounds as contrast agents for positron emission tomography (PET)[2] has spurred a vigorous research for the development of new methods for C−F bond formation under mild conditions.[3] In particular, fluorination of unsaturated carbon−carbon bonds, such as oxyfluorination,[4] aminofluorination,[5] hydrofluorination,[6] and even carbofluorination[7] of alkenes, allenes, and alkynes, has emerged as a powerful tool for C(sp^3)−F bond formation. For example, electrophilic fluorocyclization offers a convenient synthesis of fluorinated O- or N-heterocycles.[4,5] The fluorocyanation of enamines provides a facile entry to β-fluoro-α-amino acid derivatives.[7c] The Fe(III)/$NaBH_4$-mediated radical hydrofluorination of unactivated alkenes allows the incorporation of fluorine into organic substrates with an excellent functional group tolerance.[6a] However, to the best of our knowledge, no example of phosphonofluorination of any kind has ever been reported.

Phosphonates as phosphate mimics also have enormous significance in agrochemicals, pharmaceuticals, and materials.[8] Fluorinated phosphonates have thus found wide applications, especially in biomedical studies.[9] Specifically, β-fluoroalkylphosphonates exhibit a diverse range of biological activities.[10] For example, β-fluoro-α-aminoalkylphosphonates are inhibitors of alanine racemase,[10c] and the β-fluorinated phosphonate analogue of lysophosphatidic acid is an autotoxin inhibitor.[10d] However, methods for the synthesis of this important class of compounds are extremely limited.[9,10] The concomitant introduction of a fluorine atom and a phosphonyl moiety into one molecule, the phosphonofluorination of alkenes, should serve as an ideal entry to β-fluorinated phosphonates. Herein we report the first example of phosphonofluorination of unactivated alkenes.

Our idea was based on our recent finding[11] that the combination of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor reagent, Air Products and Chemicals)[12] and Ag(I) catalyst served not only as an oxidant but also as a fluorine atom transfer agent in fluorodecarboxylation of aliphatic carboxylic acids and in intramolecular radical aminofluorination of unactivated alkenes, presumably via Ag(III)F and Ag(II)F as intermediates. We envisioned that such a combination might be utilized to allow the catalytic oxidative generation of phosphonyl radicals.[13,14] As depicted in Figure 1, diethyl phosphite might be oxidized by the proposed intermediate Ag(III)F to generate Ag(II)F and a phosphonyl radical. The electrophilic phosphonyl radical then adds intermolecularly to a C=C double bond to afford the corresponding nucleophilic carbon-centered radical. Subsequent fluorine atom transfer from Ag(II)F to the adduct radical produces the phosphonofluorination product and regenerates Ag(I), which enters into the next catalytic circle. Driven by our interest in Ag(I)-catalyzed radical reactions,[11,15] we set out to explore this possibility.

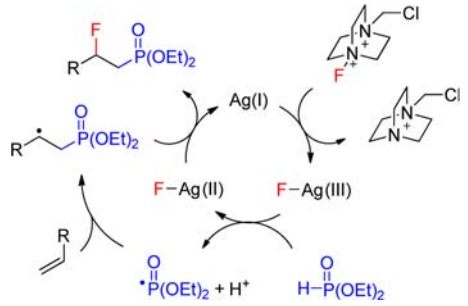

Figure 1. Proposed mechanism of radical phosphonofluorination of unactivated alkenes.

Thus, *N*-(pent-4-en-1-yl)phthalimide (**A-1**) was chosen as the model substrate for the optimization of reaction conditions (Table 1). The initial screening of solvents (entries 1−5) indicated that, under catalysis with $AgNO_3$ (20 mol %), the condensation of **A-1** with $(EtO)_2P(O)H$ and Selectfluor in CH_2Cl_2/H_2O at reflux (~40 °C) gave the expected phosphonofluorination product **1** in 18% yield, while most of the alkene **A-1** (>70%) was recovered. Note that no product **1** could be observed in the absence of water. Switching the catalyst $AgNO_3$ to AgOAc or AgOTf did not show much difference. The reaction was completely inhibited by the

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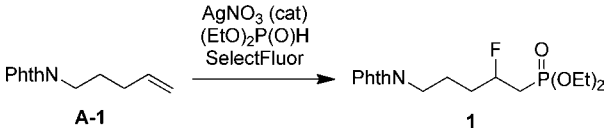
Table 1. Optimization of Reaction Conditions



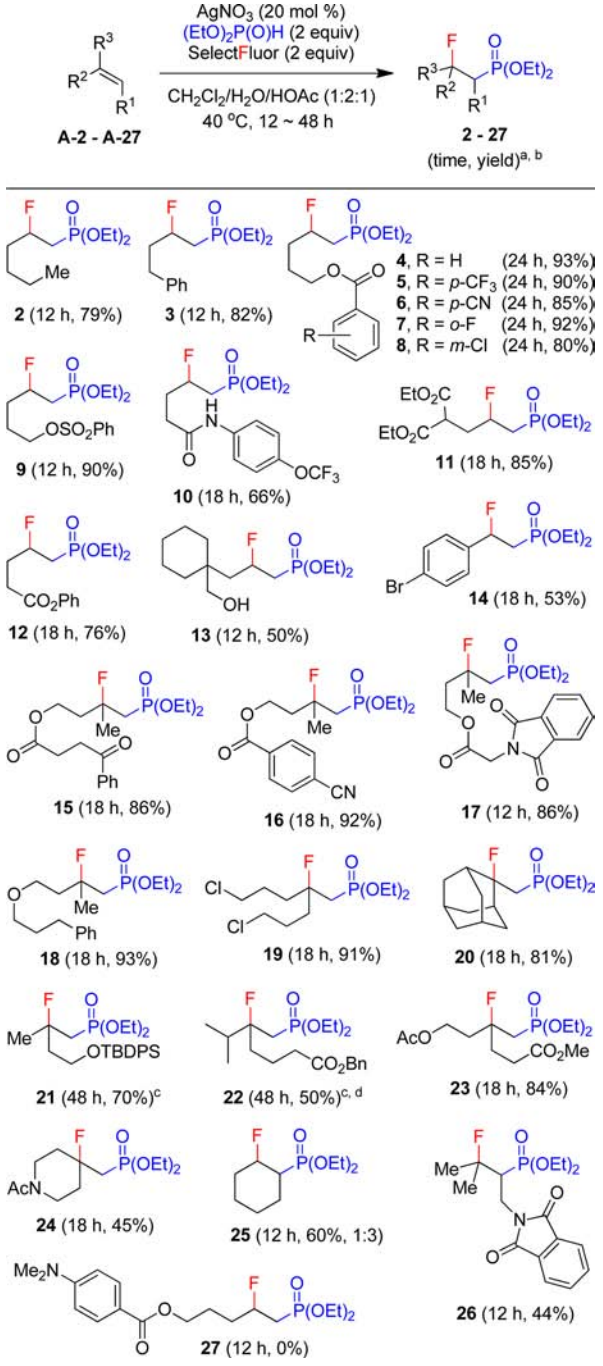
entry[a]	solvent	additive (equiv)	yield (%)[b]
1	CH_3CN/H_2O (1:1)	none	0
2	Me_2CO/H_2O (1:1)	none	0
3	C_6H_6/H_2O (1:1)	none	0
4	CH_2Cl_2/H_2O (1:1)	none	18
5	CH_2Cl_2/H_2O (1:2)	none	20
6	CH_2Cl_2/H_2O (1:2)	Na_2CO_3 (1)	0
7	CH_2Cl_2/H_2O (1:2)	HOAc (2)	20
8	CH_2Cl_2/H_2O (1:2)	TFA (5)	22
9	CH_2Cl_2/H_2O/TFA (1:2:1)	none	90
10	**CH_2Cl_2/H_2O/HOAc (1:2:1)**	**none**	**90**
11	H_2O/HOAc (2:1)	none	0
12	CH_2Cl_2/HOAc (1:1)	none	0
13[c]	CH_2Cl_2/H_2O/HOAc (1:2:1)	none	0

[a]Conditions: **A-1** (0.2 mmol), diethyl phosphite (0.4 mmol), Selectfluor (0.4 mmol), $AgNO_3$ (0.04 mmol), solvent (2 mL), 40 °C, 12 h. [b]Isolated yield based on **A-1**. [c]The reaction was run without $AgNO_3$.

addition of a base such as Na_2CO_3 (entry 6). We then turned to acids for help. The addition of a small amount (2−5 equiv) of acetic acid or trifluoroacetic acid (TFA) did not offer any improvement (entries 7 and 8). However, when acetic acid or TFA was used as the co-solvent, we were delighted to see that the phosphonofluorination proceeded cleanly, and fluoride **1** was isolated in 90% yield (entries 9 and 10). The subsequent control experiments revealed that all three co-solvents as well as the catalyst $AgNO_3$ were required for successful implementation of the reaction (entries 11−13). In addition, no reaction occurred when the fluorine source was changed to *N*-fluorobis(benzenesulfonyl)imide (NFSI). While the role of acetic acid or TFA remains unclear, it might be that the stability of the proposed Ag(III)F and/or Ag(II)F intermediates is enhanced in acidic media.

Acetic acid is obviously superior to TFA as the co-solvent in terms of the mildness of reaction conditions. Thus, the optimized conditions (entry 10, Table 1) were employed to explore the scope and limitations of the above phosphonofluorination of unactivated alkenes. The results are summarized in Scheme 1. The alkene substrate scope proved quite general, as not only various unactivated mono- and disubstituted terminal alkenes but also di- and trisubstituted internal alkenes participated in the phosphonofluorination reaction effectively. In addition, substituted styrenes could also be used as substrates, as exemplified by the synthesis of product **14**. Nevertheless, electron-deficient alkenes such as methyl acrylate failed to give the desired products. A wide range of functional groups were well tolerated, including unprotected and protected alcohol, protected amine, alkyl chloride, ether, sulfonate, ester, amide, ketone, and nitrile. However, easily oxidized groups such as phenol and unprotected amine are not compatible due to the oxidative nature of phosphonofluorination. Notably, the reaction of cyclohexene afforded the expected phosphonate **25** as a 1:3 mixture of stereoisomers in favor of the *cis*-isomer, indicating that the stereoselective phosphonofluorination could be achieved. Indeed, the reaction of 1-substituted cyclohexene **A-28** gave predominantly (~10:1) the

Scheme 1. Silver-Catalyzed Phosphonofluorination of Unactivated Alkenes



[a]Reaction conditions: alkene (0.2 mmol), diethyl phosphite (0.4 mmol), Selectfluor (0.4 mmol), $AgNO_3$ (0.04 mmol), CH_2Cl_2 (0.5 mL), H_2O (1 mL), HOAc (0.5 mL), 40 °C, 12−48 h. [b]Isolated yield based on the substrate alkene. [c]30 mol % of $AgNO_3$ was used. [d]The substrate alkene was recovered in 47% yield.

cis-addition product **28** (eq 1). A high diastereoselectivity (8:1) was also observed in the phosphonofluorination of 17-methylene steroid **A-29** (eq 2).

The above reactions could be extended to other types of phosphonyl radicals as well. As demonstrated in eq 3, diisopropyl phosphite, ethyl butylphosphinate, and even dibutylphosphine oxide all participated nicely in the phosphonofluorination under the same conditions as above without

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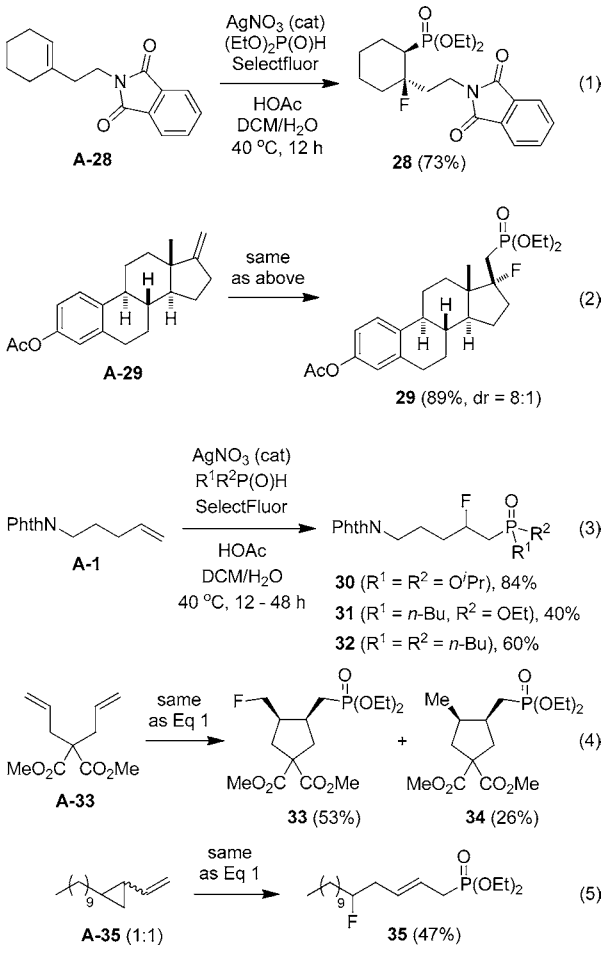

further optimization. These results further expanded the substrate scope of the reaction.

It is worth mentioning that in the synthesis of **10** and **13** no competitive electrophilic fluorocyclization[4] was observed. This also sheds light on the mechanism of phosphonofluorination, indicating it does not proceed through a carbocationic intermediate. A more direct evidence for the radical mechanism was the reaction of diene **A-33** under the above optimized conditions, which gave the cyclized products **33** (53% yield) and **34** (26% yield), both in predominantly *cis*-configuration[16] (*cis*/*trans* > 10:1) (eq 4). This result supports the radical mechanism, as the cyclized radical may abstract a fluorine atom (to give **33**) or a hydrogen atom (to give **34**). Furthermore, vinyl cyclopropane **A-35** was designed as the radical probe.[17] Indeed, the reaction of **A-35** afforded cleanly the ring-opened product **35** in 47% yield in *E*-configuration, along with the recovery of **A-35** in 37% yield. This experiment provides solid evidence for the intermediacy of carbon-centered radicals (the adduct radicals in Figure 1) in the phosphonofluorination.

To gain more insight into the role of silver catalyst in the above radical reactions, the following experiments were carried out. When divalent silver complex $Ag(Phen)_2S_2O_8$ (2 equiv) was used as the oxidant, the reaction of **A-1** with diethyl phosphite (2 equiv) and Selectfluor (2 equiv) in CH_2Cl_2/H_2O/HOAc at reflux gave only the hydrophosphorylation[14h] product in ~30% yield, while no fluoride **1** could be detected. With $K_2S_2O_8$ (2 equiv) as the oxidant and $AgNO_3$ (20 mol %) as the catalyst, the treatment of alkene **A-1** with $(EtO)_2P(O)H$ (2 equiv) and KF (2 equiv) in CH_2Cl_2/H_2O/AcOH at reflux for 12 h also led to the hydrophosphorylation of **A-1** (~50% yield) only. The reaction of **A-1** with $(EtO)_2P(O)H$ (2 equiv) and AgF_2 (2 equiv) in acetonitrile or CH_2Cl_2/H_2O/HOAc also failed to give fluoride **1**. These results, in combination with our previous finding in decarboxylative fluorination and in radical aminofluorination,[11] support the proposed mechanism in Figure 1.

In conclusion, we have successfully developed the catalytic phosphonofluorination of unactivated alkenes via condensation with diethyl phosphite and Selectfluor, leading to the convenient and efficient synthesis of β-fluorinated alkylphosphonates. The reaction proceeds under mild conditions in aqueous media and enjoys a broad substrate scope and wide functional group compatibility as well as good stereoselectivity. The above results further expand the scope of radical fluorination,[6a,11,18,19] which is emerging as a versatile and powerful tool for $C(sp^3)$–F bond formation. Furthermore, the silver-catalyzed oxidative generation of electrophilic radicals and the silver-assisted fluorine atom transfer to nucleophilic alkyl radicals illustrated in Figure 1 will allow the development of more new radical fluorination methods. This is being actively pursued in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details, characterizations of new compounds, ^1H, ^{13}C and ^{19}F NMR spectra, and complete ref 10e. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

clig@mail.sioc.ac.cn

Notes

The authors declare no competing financial interest.

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