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Short Communication

Acceleration of alkenyltrimethylsilane fluorination under mild conditions using ultrasound

Reza Ranjbar-Karimi *

Department of Chemistry, Faculty of Science, Vali-e-Asr University, Rafsanjan 77176, Islamic Republic of Iran

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ABSTRACT

Alkenyltrimethylsilanes are selectively fluorodesilated to alkenyl fluoride very readily by reaction with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis-tetrafluoroborate (Selectfluor) and *N*-fluorobenzensulfonimids at room temperature under ultrasound. In the presence of ultrasound irradiation in the case of one of the reactions, the yield was 85% after 25 min, but using the previously established thermal method the yield was only 32% after 20 h.

1. Introduction

The introduction of fluorine into organic compounds changes dramatically the physical and biological properties and chemical reactivity of organic materials. Selective fluorination under mild reaction conditions using electrophilic reaction processes is one of the most important strategies in organic synthesis. Various electrophilic fluorinating reagents have been developed and evaluated, and, in each case, optimum reagents have been selected and used for each individual purpose. N–F reagent, in particular Selectfluor reagent, is one of the best general-purpose user-friendly electrophilic fluorinating agents [1–4].

The effect of ultrasound on different reactions has been widely studied during the last two decades [5–7]. The application of ultrasound to chemical reactions can cause an increase in the yields of reactions and in some cases the ratio of products formed. The most important effect when ultrasound passes through a liquid medium is the generation of many cavities. This leads to high temperatures and high pressures within the cavities during their collapse.

Previously we reported the use of ultrasound irradiation for electrophilic fluorination of CH and CH_2 groups attached to heterocyclic and nitro functionalities [8]. In this work we have established new methodologies for the selective preparation of some alkenyl fluorides by the reaction of corresponding alkenyltrimethylsilanes compounds with electrophilic fluorinating agents under ultrasonic irradiation.

There is a recent report on the use of electrophilic fluorination for the preparation of alkenyl fluoride from corresponding organometallic compounds in low yield and long reaction times [9].

2. Experimental

2.1. Materials

1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis-tetrafluoroborate (Selectfluor™, abbreviated Selectfluor) and *N*-fluorobenzensulfonimids was purchased from Aldrich. Alkenyltrimethylsilanes have been prepared according to the reported procedure [10].

2.2. Equipments

The ultrasonic device used was an UP 400 S instrument from Dr. Hielscher GmbH. An S3 immersion horn emitting 24 kHz ultrasound at intensity levels tunable to maximum sonic power density of 460 W cm^{-2} was used. Sonication was carried out at 100% (maximum amplitude 210 μm). A 3 mm long sonotrode (maximum immerse depth of 90 mm) was immersed directly into the reaction mixture. NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 475 MHz for ^{19}F with trifluorochloromethane as an internal standard. Thin layer chromatography (TLC) was run on silica percolated aluminium plates (Merck Kieselgel

* Tel.: +98 391 3202162; fax: +98 391 3202427.
E-mail address: karimi_r110@yahoo.com

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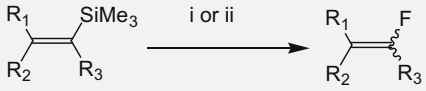
Table 1
Fluorodesilylation of alkenyltrimethylsilanes.



1a-i **2a-i**

Entry	Products	R_1	R_2	R_3	% Yield (time/min)[a,e]	% Yield (time/min)[b,e]	% Yield (time/h)[c,e]
1	2a	H	C_6H_5	H	85 (25)	80 (30)	32 (20)[d]
2	2b	H	*p*-MeC_6H_4	H	87 (25)	85 (25)	34 (21)
3	2c	H	*p*-ClC_6H_4	H	88 (25)	80 (25)	30 (20)
4	2d	H	C_6H_5	C_6H_5	85 (30)	82 (30)	35 (23)
5	2e	Br	C_6H_5	H	85 (30)	76 (30)	48 (22)
6	2f	C_6H_5	H	H	90 (30)	84 (35)	32 (20)
7	2j	Et	C_6H_5	H	80 (30)	80 (40)	57 (21)[d]
8	2h	H	*n*-C_6H_{13}	H	75 (30)	70 (35)	45 (22)[d]
9	2i	H	*n*-C_4H_9	H	80 (35)	83 (40)	29 (23)

[a] *Conditions i:* Selectfluor, CH_3CN.
[b] *Conditions ii: N*-fluorobenzensulfonimids, CH_3CN.
[c] Selectfluor, CH_3CN, stirring at room temperature (without sonication).
[d] According to Ref. [9].
[e] All compounds were obtained as Z/E mixtures and identified by comparison of their physical and spectral data with those of authentic samples.

F254). Melting points were determined on a Kofler hot-stage apparatus.

2.3. General procedure for fluorodesilylation reactions

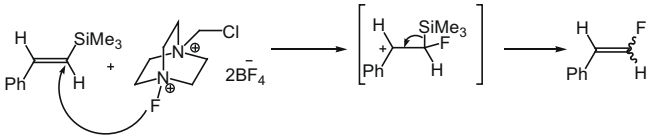
Conditions i: To a solution of the appropriate alkenyltrimethylsilane compound (2.9 mmol) in dry CH_3CN (10 mL) was added selectfluor (2.9 mmol 1.02 g). The reaction mixture was irradiated with ultrasound for 25–35 min. The mixture was filtered and poured into saturated aqueous sodium hydrogen carbonate (20 ml) and extracted with diethyl ether (2 × 20). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$, filtered and the solvent was removed. The product was purified on a silica column eluted with a 1:1 mixture of dichloromethane and hexane.

Condition ii: To a solution of the appropriate alkenyltrimethylsilane compound (2.9 mmol) in dry CH_3CN (10 mL) was added *N*-fluorobenzensulfonimids (2.9 mmol, 0.68 g). The reaction mixture was irradiated with ultrasound for 25–40 min. The mixture was filtered and poured into saturated aqueous sodium hydrogen carbonate (20 ml) and extracted with diethyl ether (2 × 20). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$, filtered and the solvent was removed. The product was purified on a silica column eluted with a 1:1 mixture of dichloromethane and hexane.

The authenticity of the products was established by comparing their melting points with the data in the literature and ^1H NMR spectra.

3. Results and discussion

We have utilized the commercially available 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis-tetrafluoroborate (Selectfluor™, abbreviated Selectfluor) and *N*-fluorobenzensulfonimids as fluorinating agents. Table 1 summarizes the yield of the reactions using these two new methods. The expected fluoroalkenes **2a–i** were obtained as *Z*/*E* mixtures in good yields. It is clear that reactions of **1** with these electrophilic fluorinating reagents under ultrasonic irradiation are much more selective and have shorter reaction times. For example, compound **2a** (entry 1) was previously prepared in 32% yield in the presence of 1 eq selectfluor in acetonitrile at room temperature after 20 h [9], whereas under sonication **2a** was obtained in 85% at room temperature within 25 min. In terms of the mechanism, the reaction of **1** to form **2** might involve an addition–elimination pathway via a carbocationic intermediate (Scheme 1).



Scheme 1. The reaction of **1** to form **2** mechanism.

4. Conclusion

In conclusion, the use of ultrasound enabled the easy preparation of alkenyl fluorides by reaction of corresponding alkenyltrimethylsilanes compounds with electrophilic fluorinating agents. The advantages of ultrasound in fluorination are shorter reaction times and higher yields.

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