



Alternative synthetic routes to hydrofluoroolefins



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ABSTRACT

A series of hydrofluoroolefins with $-\text{CF}=\text{CH}_2$, $-\text{CH}=\text{CHF}$ and $-\text{CH}=\text{CF}_2$ groups were designed and prepared via various synthetic routes, including HX or BrF elimination, Wittig-type olefination or fluorination using SF_4 .

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1. Introduction

While it has not been proven, most climate scientists agree that global climate change is the result of the release of large amounts of CO_2 from the burning of fossil fuels with a contribution from long lived man-made chemicals that accumulate in the upper atmosphere and absorb infrared radiation from the Earth [1]. Traditional fluorochemicals have high global warming potentials, and many are used in emissive applications. Hence, low global warming alternatives are constantly being sought after that have the appropriate characteristics and physical properties for end use applications such as refrigeration, air conditioning, foam expansion, clean agent fire suppression, specialty fluids, propellants, and semiconductor chip manufacture [2]. The industry has been targeting hydrofluoroolefins for these applications since the unsaturation reduces atmospheric life by providing a point of attack for hydroxyl and nitroxyl radicals [3]. Our efforts have been focused on identifying and developing synthetic schemes to hydrofluoroolefin candidates that are economically viable, have low toxicity, low cost of manufacture, appropriate level of flammability, and efficacy in use.

Traditional Swarts chemistry while useful is of limited utility in the synthesis of functionalized olefins. The products of this type of reaction are usually saturated and have some chlorine remaining in the molecule [4], which can lead to a high ozone depletion potential. Herein we examine Br–F elimination reactions, fluorinations with SF_4 , Wittig-type olefinations, and HX elimination as more selective methods to make hydrofluoroolefins.

2. Results and discussion

2.1. Polyfluoroalkenes with $-\text{CF}=\text{CH}_2$ fragment

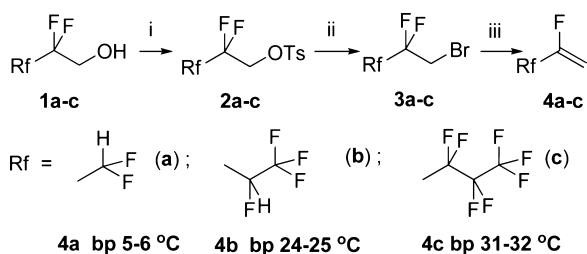
2.1.1. Elimination reactions

The elimination reaction is a common method to access olefins with $-\text{CF}=\text{CH}_2$ fragment by few ways.

2.1.1.1. BrF elimination. Some olefins were obtained via this method from fluorinated alcohols $\text{R}_f\text{CF}_2\text{CH}_2\text{OH}$, which were activated with tosyl chloride to give tosylates [5], which were transformed into appropriate bromides with KBr [6]; the last were treated with Zn to eliminate BrF [7] and afford desired olefins. Three alkenes – 2,3,3-trifluoroprop-1-ene (**4a**), 2,3,4,4,4-pentafluorobut-1-ene (**4b**) and 2,3,3,4,4,5,5,5-octafluoropent-1-ene (**4c**) were prepared in such a way according to Scheme 1:

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Scheme 1. Syntheses of alkenes **4a–c** from appropriate alcohols, *reagents and conditions:* (i) an equimolar mixture of alcohol **1a–c**, TsCl and base, rt, yields 75–90%; (ii) excess KBr, diethylene glycol, 200 °C, yields 70–80%; (iii) 3-fold excess of activated Zn metal, iso-propanol or dioxane, reflux, yields: **4a** – 81%, **4b** – 63%, **4c** – 82%.

2.1.1.2. HX elimination. This synthetic approach to terminal fluorinated alkenes is widely used. Tosylation of an appropriate alcohol followed by a base-promoted elimination of *p*-toluenesulfonic acid (PTSA) affords polyfluoroalkenes with good yields [8]. The preparation of 1-fluoro-1-(pentafluoroethoxy)ethene (**7**) was performed with this strategy according to **Scheme 2**:

Alcohol **5** was converted into its tosylate **6** using a typical procedure [5] followed by treatment with an equimolar amount of LiHMDS. We were not successful using either *t*-BuOK, DBU or KF [8] for abstraction of PTSA.

Starting compound **5** was prepared using two-step process depicted by **Scheme 3**:

Ethyl bromofluoroacetate (**8**) was reacted with cesium alkoxide (**9**) [9] to produce the ester **10** in a moderate yield, followed by the reduction using LiAlH₄ to afford alcohol **5**.

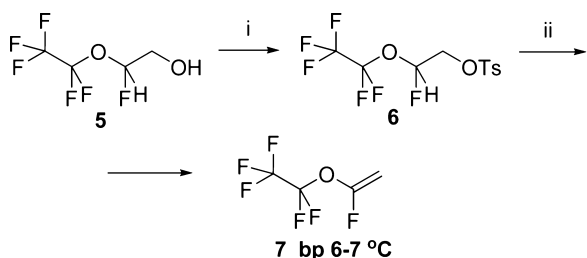
It should be noted, that an alternative synthetic route to ester **10** using the reaction of **8** with *N*-fluoro(phenylsulfonyl)imide (NFSI) resulted in low yield formation of acetate **10** (NMR data) in a mixture with starting ester **11** (**Scheme 4**).

2.1.2. Fluorination of β -diketones with SF₄

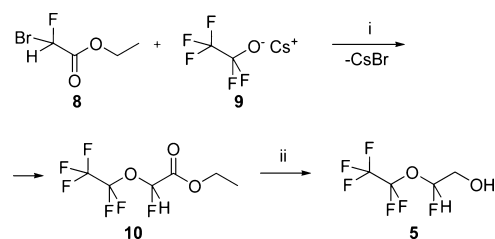
Inspired by the work of Lev Yagupolskii and coworkers [10] on the fluorination of β -diketones with SF₄, 2,3,3,4,4-pentafluorobut-1-ene (**13**) was prepared from β -diketone **12** (**Scheme 5**).

β -Diketone **12** was obtained from ethyl 2,2,3,3-tetrafluoropropanoate and acetone through a classic Claisen condensation [11]. Fluorination occurred in accordance with a scheme, proposed by Yagupolskii to give the expected olefin **13** in a satisfactory yield. The isolated olefin **13** was contaminated by-product 1,1,1-trifluoroethane (~7 molar%, based on NMR and GLC).

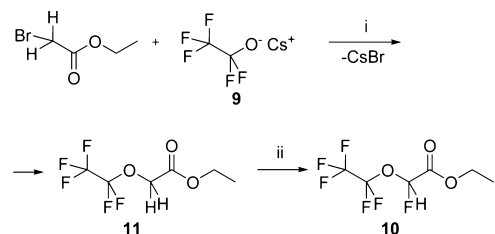
In order to increase the number of alkenes, accessible by this approach, an attempt was made to synthesize the aforementioned isomeric olefin **4b**. (3*Z*)-5,6,6,6-tetrafluoro-4-hydroxyhex-3-en-2-one (**16**) has been obtained previously in a moderate yield ($\leq 40\%$) by electrophilic acylation of trifluoroethene with acetyl fluoride



Scheme 2. Synthesis of alkene **7** from alcohol **5** by subsequent tosylation and elimination of PTSA. *Reagents and conditions:* (i) equiv. of TsCl, Py, as a base and a solvent, 0 °C \rightarrow rt, 12 h, yield 82%; (ii) equiv. of LiHMDS, DME, rt \rightarrow 100 °C, 4 h, yield 57%.



Scheme 3. Synthesis of alcohol **5**. *Reagents and conditions:* (i) an equimolar mixture of **8** and **9**, DME, rt, overnight, then 50 \rightarrow 80 °C, 4 h, yield 45%; (ii) LiAlH₄, ether, reflux, 1 h, yield 68%.

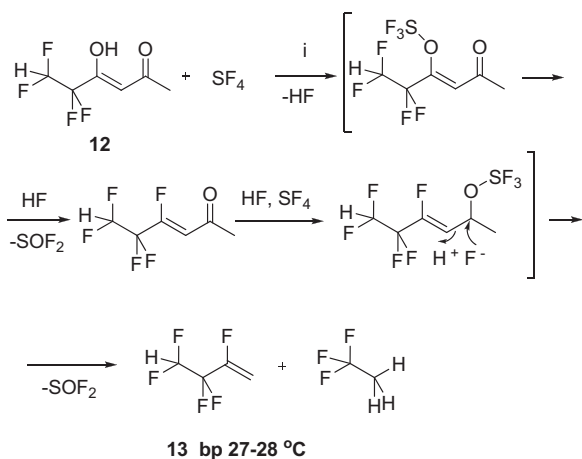


Scheme 4. An alternative synthesis of ester **10** via electrophilic fluorination with NFSI. *Reagents and conditions:* (i) an equimolar mixture of reagents, DME, rt overnight, then 50 \rightarrow 80 °C, 4 h, yield 63%; (ii) an equimolar mixture of BuLi, NFSI and **11**, THF/hexane, -90 °C, 4 h, -90 °C \rightarrow rt, overnight, yield ~30%, as a mixture **11/10** \approx 2/1.

using SbF₅ catalyst [12]. Since classical Claisen methodology cannot be used due to dehydrofluorination under basic conditions, an alternative route was employed to prepare diketone **16** (**Scheme 6**).

Synthesis was carried out by the reaction of 2,3,3,3-tetrafluoropropanoyl chloride (**14**) [13] and 2-methoxyprop-1-ene resulting in vinyl ether **15**, followed by a hydrolysis step to give the desired β -diketone **16** in a high yield. It should be noted that this ketone exists in solution only in the enol form, which is typical for fluorinated β -diketones.

It turned out that the method of β -diketones fluorination with SF₄ is inapplicable for the synthesis of butene **4b**. Fluorination of enole **16** occurred without cleavage of the chain, giving a complex mixture of fluorinated products (**Scheme 7**).



Scheme 5. Synthesis of alkene **13** via fluorination of β -diketone **12** with SF₄. *Reagents and conditions:* autoclave, 2-fold excess of SF₄, without solvent, 80 °C, 20 h, yield 58%, impurity CF₃CH₃ ~7 molar%.

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