Journal of Fluorine Chemistry 144 (2012) 79–85

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

# Siloxane based syntheses of fluorous ethenes and their tandem Heck reactions with aryl iodides

Ágnes Csapó, József Rábai *

*Institute of Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518, Budapest 112, Hungary*

ARTICLE INFO

*Article history:*
Received 25 June 2012
Received in revised form 18 July 2012
Accepted 19 July 2012
Available online 27 July 2012

*Keywords:*
Phosphine-free Heck reaction
Protodesilylation
Fluorous styrenes
Silica bonded 'fluorous ethene equivalent'

ABSTRACT

Perfluoroalkyl-ethenes ($R_{fn}CH{=}CH_2$, **6a–c**; **a**, $n = 4$; **b**, $n = 6$; **c**, $n = 8$) were prepared in good isolated yields (67–89%) and high purity (GC assay > 98%) from various fluorinated organosilanes in fluoride-anion assisted protodesilylation reactions. The environmentally more benign '$KF/NEt_3/H_2O$' reagent combination introduced here was found as an effective substitute for the commonly used tetrabutylammonium-fluoride trihydrate ($TBAF{\cdot}3H_2O$) as a fluoride source. Fluorous styrenes ((*E*)-$R_{fn}CH{=}CH{-}Ar$, **8**) were then prepared in good isolated yields (58–93%/iodoarene) and purities (GC assay > 95%) with the Pd(0) catalyzed Heck coupling of iodoarenes (Ar-I, **7**) and perfluoroalkyl-ethenes generated *in situ* by the fluoride assisted cleavage of (β-perfluoroalkyl-α-iodo-ethyl)-siloxane ($[R_{fn}CH_2CH(I)SiMe_2]_2O$, **3**) precursors in DMF solution at elevated temperatures. They are accessible by the one-pot reaction of dimethylvinylchlorosilane ($CH_2{=}CHSiMe_2Cl$, **2**) and perfluoroalkyl iodides ($R_{fn}$-I, **1**) as we reported earlier. Similarly, the radical chain addition of $C_8F_{17}I$ to $CH_2{=}CHSi(OMe)_3$ (**9**) gave (β-perfluorooctyl-α-iodo-ethyl)-trimethoxysilane ($[C_8F_{17}CH_2CH(I)]Si(OMe)_3$, **10**) in good yield, which then was reacted with silica gel in dry toluene to obtain an $SiO_2$-bonded (perfluorooctyl)ethene surrogate [*silica*$({-}O{-})_3Si{-}CH(I)CH_2C_8F_{17}$, **11**]. The fluoride assisted cleavage of **11** and tandem Heck reaction with iodobenzene afforded the appropriate cross-coupled product (*E*)-$C_8F_{17}CH{=}CHPh$.

## 1. Introduction

Organosilicon reagents are widely used in synthetic organic chemistry, most frequently as protecting groups for alcohols. Soluble fluorides or some acids selectively remove the silyl groups when the protection is no longer needed [1]. This reaction is often a $F^-$ assisted cleavage reaction which is also called as protodesilylation.

The most common reagent for this purpose is tetrabutylammonium fluoride which commercially available in the form of trihydrate ($TBAF{\cdot}3H_2O$) or as a stock solution in THF. Terminal alkynes could be generated by the fluoride assisted cleavage reaction of the corresponding $RC{\equiv}CSiR_3$ precursors [2]. β-Perfluoroalkyl-α-iodoalkyl-silanes easily undergo dehydrohalogenation with $NEt_3$ to afford (*E*)-$C_nF_{2n+1}CH{=}CHSiMe_3$ type alkenyl silanes [3], or can be cleaved with $TBAF{\cdot}3H_2O$ in a simultaneous protodesilylation/dehydrohalogenation process to give $C_nF_{2n+1}CH{=}CH_2$ fluorous ethenes (Scheme 1; Q = $SiMe_3$) [4].

The palladium-catalyzed C–C coupling between aryl or vinyl halides and activated alkenes in the presence of a base is referred as the Heck reaction [5]. Recent developments both in the catalysts and reaction conditions have resulted in a much broader range of donors and acceptors allowing this reaction. One of the benefits of involving Heck reaction in a synthetic strategy is its outstanding *trans*-selectivity [6].

Heck and other cross-coupling reactions have been instrumental for the development of *metal-catalyzed organic syntheses* [7]. The Heck reaction became an effective synthetic tool for *fluorous chemistry* as well [8]. Palladium catalyzed olefination of haloarenes with perfluoroalkyl-ethenes provides a convenient means for the synthesis of fluorous aromatics [9]. Fluorous aryl compounds were obtained by the arylation of olefins with an arenediazonium salt by the cross-coupling of classical $ArN_2X$ with $C_nF_{2n+1}CH{=}CH_2$ at room temperature in methanol [10].

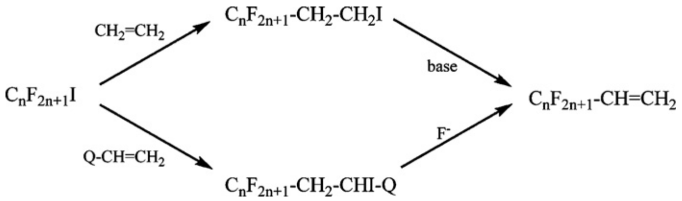
Here we disclose a new approach for the preparation of fluorous aromatic compounds by Heck reaction, which is based on the *in situ* generation of fluorous olefins using easily accessible silane or disiloxane precursors. Such perfluoroalkyl-ethenes ($C_nF_{2n+1}CH{=}CH_2$) have been manufactured in a two-step procedure starting with the radical addition of perfluoroalkyl iodides to ethene in a pressure autoclave [11], which then was followed by the dehydroiodination of the (perfluoroalkyl)ethyl iodide intermediates with a suitable base (Scheme 1, upper path) [12].

Perfluoroalkyl-iodides ($n$-$C_nF_{2n+1}I$, $R_{fn}I$, $n = 2$–14) with even number of carbons are common sources of perfluoroalkyl-groups [13], which became the ultimate precursors for the synthesis of fluorous compounds [14].

---

* Corresponding author. Tel.: +36 1 372 2500; fax: +36 1 372 2592.
*E-mail address:* rabai@elte.hu (J. Rábai).

0022-1139/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jfluchem.2012.07.010



**Scheme 1.** Alternative syntheses of fluorous ethenes (Q = $SiMe_3$, $SiMe_2X$, . . .).

In this paper we aimed to generalize the above findings by expanding the scope of the fluoride ion assisted cleavages of appropriate silanes and siloxanes for the preparation and/or *in situ* generation of terminal fluorous alkenes *via* combined dehydrohalogenation protodesilylation (Scheme 1; Q = -$SiMe_2Cl$ or (-$SiMe_2$)$_2$O).

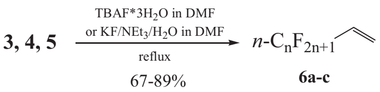
## 2. Results and discussion

We reported earlier a three step synthesis to fluorous alkenylfluorosilanes (Scheme 2) [15].

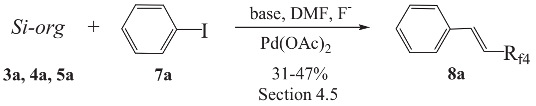
These silanes (**3**–**5**) were tested in a protodesilylation-reaction with different reagents. First TBAF·$3H_2O$ was used to generate the appropriate perfluoroalkyl-ethenes **6a**–**c**, as it is the most commonly used fluoride source in these reactions (Scheme 3).

It was found that all three organosilanes (**3a**, **4a** and **5a**) undergo protodesilylation successfully in the presence of TBAF·$3H_2O$ in DMF (Table 1, entries 1–3). Since β-perfluoroalkyl-α-iodo-siloxanes **3** can be made in a one step procedure (Scheme 2), we selected them for further studies instead of **4** and **5**. We tried to replace TBAF·$3H_2O$ with more environmentally benign reagents for the protodesilylation of **3**. These experiments revealed that the KF/$NEt_3$/$H_2O$ triad in DMF have the same or better efficiency as TBAF·$3H_2O$ if at least stochiometric amount of water was present (Table 1, entries 4–6). It is noteworthy that without water the protodesilylation reaction does not take place. These experiments explicitly prove that water behaves as a proton source and the added water does not compromise nucleophilicity of the fluorides supplied by potassium fluoride. The appropriate olefins were isolated in excellent yields and purities using co-distillation with pyridine [16].

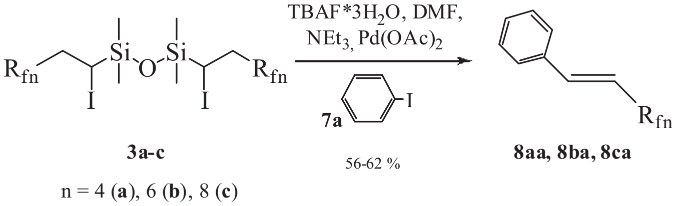
These protodesilylation reactions using KF/$NEt_3$/$H_2O$ triad are more environmentally benign and less expensive than the commonly used reactions with quaternary ammonium salts whereas provide the same efficiency.



**Scheme 3.** Preparation of fluorous ethenes *via* protodesilylation.



**Scheme 4.** Tandem Heck-reactions with different olefin-sources.



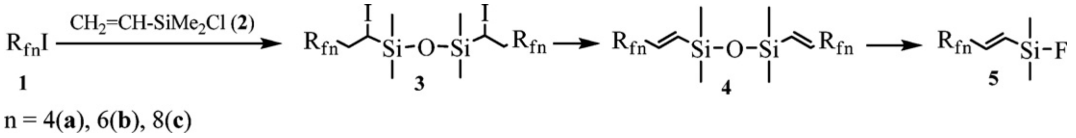
**Scheme 5.** Tandem Heck coupling of **3a**–**c** with $C_6H_5I$ in the presence of TBAF·$3H_2O$/$NEt_3$.

Next ligand-free tandem Heck reactions with iodobenzene substrate were developed using the above protodesilylation methods for the *in situ* generation of the olefin partners. First all the three organosilicon based (perfluorobutyl)ethene precursors (**3a**, **4a** and **5a**) were tested using TBAF·$3H_2O$ as fluoride source, $Pd(OAc)_2$ as catalyst and $NEt_3$ as a base in DMF solvent (Scheme 4).

All the three couplings were successful and styrene **8a** was isolated in 31–47% yields without optimization. This new tandem Heck reaction may have some advantages compared to those performed directly with olefins, since our silicon based olefin precursors are easy to handle and less volatile liquids with long shelf-life.

Since olefin precursors **3a**, **4a** and **5a** gave similar isolated yields in the Heck coupling reaction, for further studies compounds **3a**–**c** were chosen again. We have found that the length of the perfluoroalkyl groups has no significant effect on the yield of the coupling reaction (Scheme 5).

Then we replaced the traditional TBAF·$3H_2O$ as a fluoride source with the KF/$NEt_3$ reagent pair in the next coupling reactions, since the latter reagent combination showed similar reactivity in the protodesilylation step. We have found that the KF/$NEt_3$ system have the same reactivity in the coupling reaction, too. We observed

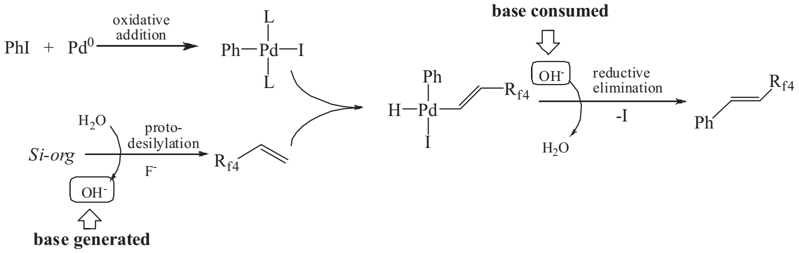


**Scheme 2.** Preparation of fluorous organosilanes from perfluoroalkyl-iodides.

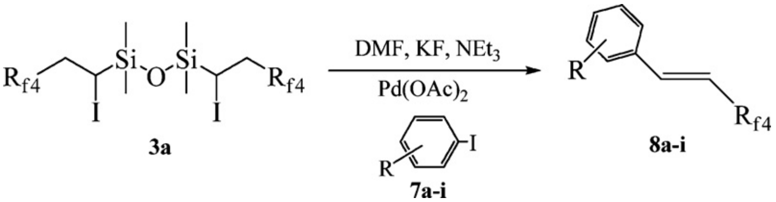
**Table 1**
Olefin generation from organosilanes using different reagents.

| Entry | Organosilane | Reagents | Isolated yield (%) | GC purity (%) | Product |
|---|---|---|---|---|---|
| 1 | $R_{f4}$–CH=CH–$SiMe_2F$ (5a) | TBAF·$3H_2O$ | 89[a] | 98 | $R_{f4}$–CH=$CH_2$ (6a) |
| 2 | ($R_{f4}$–CH=CH–$SiMe_2$)$_2$O (4a) | TBAF·$3H_2O$ | 75[a] | 98 | $R_{f4}$–CH=$CH_2$ (6a) |
| 3 | ($R_{f4}$–$CH_2$–CHI-$SiMe_2$)$_2$O (3a) | TBAF·$3H_2O$ | 73[a] | 98 | $R_{f4}$–CH=$CH_2$ (6a) |
| 4 | ($R_{f4}$–$CH_2$–CHI-$SiMe_2$)$_2$O (3a) | KF/$NEt_3$/$H_2O$ | 67[b] | 98 | $R_{f4}$–CH=$CH_2$ (6a) |
| 5 | ($R_{f6}$–$CH_2$–CHI-$SiMe_2$)$_2$O (3b) | KF/$NEt_3$/$H_2O$ | 70[b] | 99 | $R_{f6}$–CH=$CH_2$ (6b) |
| 6 | ($R_{f8}$–$CH_2$–CHI-$SiMe_2$)$_2$O (3c) | KF/$NEt_3$/$H_2O$ | 83[b] | 98 | $R_{f8}$–CH=$CH_2$ (6c) |

[a] Isolation with distillation.
[b] Isolation with distillation and pyridine-codistillation.



**Scheme 6.** Expected mechanism of the tandem Heck reaction.



**Scheme 7.** Tandem Heck-reaction of **3a** with different iodoarenes **7a–i** in the presence of KF/NEt$_3$.

that no equivalent amount of water have to be used during the tandem generation and coupling reaction of the perfluoroalkylethene intermediates, since the presence of only catalytic amount of water is satisfactory as it is regenerated in the last – reductive elimination – step of the catalytic cycle (Scheme 6).

Next the effect of the substituents of iodobenzenes (**7a**–**i**) was tested using **3a** in the presence of KF/NEt$_3$ and Pd(OAc)$_2$. Substituted fluorous styrenes (**8a**–**i**) were isolated in good to excellent yields (58–93%). However, our effort to expand the scope to bromobenzene failed even in the presence of added PPh$_3$ (2 eq to Pd(OAc)$_2$) or using other catalysts (Pd$_2$dba$_3$, Pd(PPh$_3$)$_4$, (allyl-Pd-Cl)$_2$) at 100 °C (Scheme 7 and Table 2).

An important requirement in the synthesis design is to avoid the formation of co-products. Although separation of styrenes **8a**–**i** from the low-boiling organosilanes generated as by-products was not troublesome, this step might be problematic in other similar reactions affording more volatile target molecules. For ideal separation of products and other reaction components after a complete reaction the purposeful use of orthogonal phases should be considered. Liquid–gas, solid–liquid, solid–gas and aqueous–organic or organic–fluorous liquid–liquid phases are the best known examples and generally accepted for strategy-level separations [17].

Here we disclose the synthesis of a novel functionalized fluorous silica gel (**11**), which on the one hand could be used as a solid phase supported (perfluoroalkyl)ethene precursor, or on the other hand following the reductive removal of the α-iodine substituent could open up novel routes for the synthesis of fluorous silica gels [18].

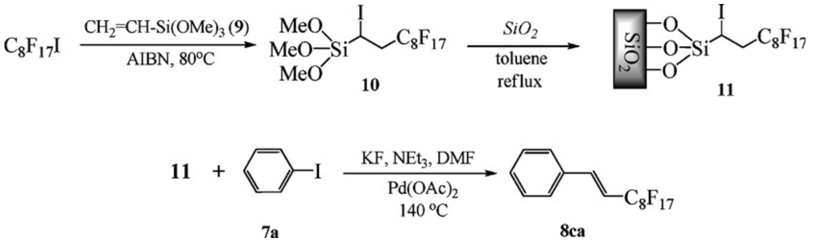
The synthesis of reagent **11** is shown in Scheme 8. In the first step C$_8$F$_{17}$I was reacted with trimethoxyvinylsilane (**9**) in the presence of AIBN [19]. After the reagent was immobilized on silica gel its load was calculated from microanalytical I% data. The reaction of the immobilized reagent **11** and iodobenzene was successful; the expected product (**8ca**) was isolated in 47% yield and 96% purity as determined by GC. The co-product formed in this reaction remains bonded to silica and can be removed by filtration (*cf.* Section 4). Silica does not disturb this tandem coupling reaction similarly to many reported techniques using supported reactants and catalysts for Heck coupling reactions [20].

Finally we have tested if these reactions could have a transmetallation step based mechanism which is characteristic to Hiyama type mechanism. In opposite to the Heck mechanism (Scheme 9, lower path) no base is required to proceed Hiyama's transmetallation mechanism (Scheme 9, upper path).

With disiloxane **4a** and fluorosilane **5a** no significant difference in the yields and reaction times was seen in the absence or presence of the base, because their protodesilylation reaction gave an equivalent amount of OH$^-$, which in turn could react as a base to assist HX elimination in the last step of the reaction (see Scheme 6).

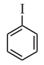
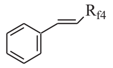
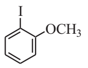
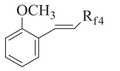
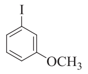
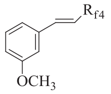
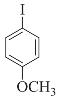
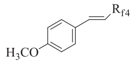
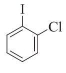
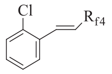
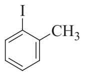
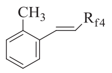
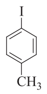
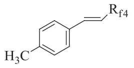
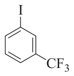
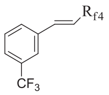
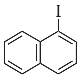
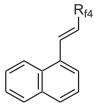
In case of α-iodoethylsiloxane **3a**, the difference was significant, since here one equivalent of acid (HI) is formed simultaneously during the protodesilylation, which neutralizes the formed OH$^-$ base (Scheme 10, Eq. (1)). In the presence of NEt$_3$ the reaction takes place with 100% conversion, while in the absence of that, the reaction fails (0% conversion to iodobenzene; *cf.* Section 4.5, *Condition B*).

These results strongly support our prediction, that these reactions have a tandem Heck type mechanism, because if the Hiyama type transmetallation step would be involved, than the

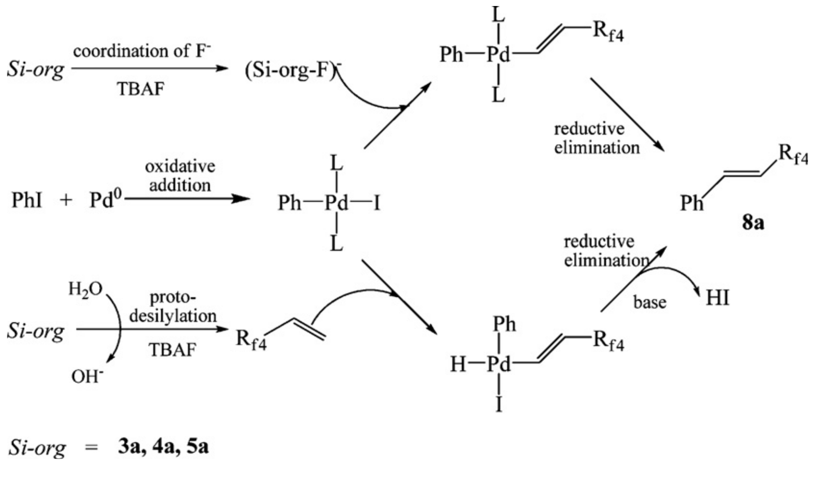


**Scheme 8.** Tandem Heck-reaction with a functionalized fluorous silica gel.

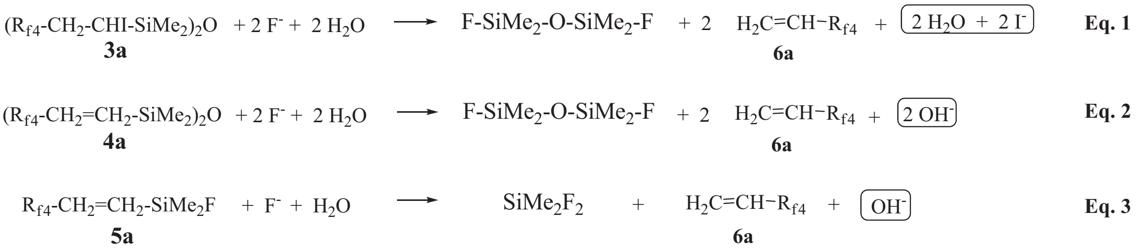
**Table 2**
Tandem Heck reaction of iodoarenes (**7a–i**) with β-(perfluorobutyl)-α-iodoethyl-siloxane (**3a**).

| Entry | Iodoarene | Yield (%) | GC purity (%) | Product | References[a] |
|---|---|---|---|---|---|
| 1 | <br>(**7a**) | 60 | 95% | <br>(**8a**) | [15] |
| 2 | <br>(**7b**) | 85 | 96% | <br>(**8b**) | n.c. |
| 3 | <br>(**7c**) | 66 | 95% | <br>(**8c**) | [15]. |
| 4 | <br>(**7d**) | 63 | 95% | <br>(**8d**) | [15] |
| 5 | <br>(**7e**) | 70 | 95% | <br>(**8e**) | n.c. |
| 6 | <br>(**7f**) | 93 | 95% | <br>(**8f**) | [15] |
| 7 | <br>(**7g**) | 67 | 95% | <br>(**8g**) | [15] |
| 8 | <br>(**7h**) | 58 | 95% | <br>(**8h**) | [15] |
| 9 | <br>(**7i**) | 75 | 95% | <br>(**8i**) | [15] |

[a] n.c. = new compound.



**Scheme 9.** Possible routes to the formation of fluorous syterenes – upper path: Hiyama type mechanism with a transmetalation step; lower path: tandem Heck type mechanism.



$$\underset{\mathbf{3a}}{(R_{f4}\text{-}CH_2\text{-}CHI\text{-}SiMe_2)_2O} + 2\,F^- + 2\,H_2O \longrightarrow F\text{-}SiMe_2\text{-}O\text{-}SiMe_2\text{-}F + 2\;\underset{\mathbf{6a}}{H_2C{=}CH{-}R_{f4}} + \boxed{2\,H_2O + 2\,I^-} \quad \textbf{Eq. 1}$$

$$\underset{\mathbf{4a}}{(R_{f4}\text{-}CH_2{=}CH_2\text{-}SiMe_2)_2O} + 2\,F^- + 2\,H_2O \longrightarrow F\text{-}SiMe_2\text{-}O\text{-}SiMe_2\text{-}F + 2\;\underset{\mathbf{6a}}{H_2C{=}CH{-}R_{f4}} + \boxed{2\,OH^-} \quad \textbf{Eq. 2}$$

$$\underset{\mathbf{5a}}{R_{f4}\text{-}CH_2{=}CH_2\text{-}SiMe_2F} + F^- + H_2O \longrightarrow SiMe_2F_2 + \underset{\mathbf{6a}}{H_2C{=}CH{-}R_{f4}} + \boxed{OH^-} \quad \textbf{Eq. 3}$$

**Scheme 10.** Stoichiometric representation of the protodesilylations (*cf.* Section 4.5).

reaction of **3a** would have been completed to afford the fluorous styrene $R_{f4}CH{=}CHPh$ (**8a**), even in the absence of the base (*cf.* Scheme 9).

## 3. Conclusions

Easily accessible β-(perfluoroalkyl)-α-iodoethyl-disiloxanes and related fluorous organosilanes were used for the generation of (perfluoroalkyl)-ethenes using more environmentally benign reagents for protodesilylations.

Experimental evidence was given that the reaction of iodobenzenes and the above fluorous organosilicon derivatives under specified condition could afford ω-perfluoroalkyl-styrenes in good yields involving an unusual fluoride-induced elimination–desilylation tandem Heck type mechanism.

A new functionalized fluorous silica gel was developed as an orthogonal solid phase (perfluoroalkyl)-ethene precursor to simplify product separations.

## 4. Experimental

### 4.1. Materials and methods

Palladium(II)-acetate (99.9+%) and TBAF ($Bu_4NF{\cdot}3H_2O$) were purchased from Alfa Aesar. The other reagents and solvents were purchased from Alfa Aesar or Molar (Hungary). Organosilicon reagents (**3**–**5**) were synthesized as reported [15]. DMF was distilled from $CaH_2$ prior to use. Fluka Silica gel 60 (60,739) was used for flash column chromatography and as support material. NMR spectra were recorded at 298 K on Bruker Avance 250 MHz spectrometer equipped with a QNP $^1H/^{13}C/^{19}F/^{31}P$ probe-head. $^1H$ and $^{13}C$ spectra were referenced to the signal of chloroform. Chemical shifts ($\delta$) are given in parts per million (ppm) units relatively to the internal standard TMS ($\delta = 0.00$ for $^1H$, $\delta = 0.00$ for $^{13}C$) and to $CFCl_3$ as external standard ($\delta = 0.00$ for $^{19}F$). GC analyses were performed on a Hewlett–Packard 5890 Series II chromatograph, Column: PONA [crosslinked methylsilicone gum], 50 m × 0.2 mm × 0.5 μm, carrier gas: $H_2$, FID detection (detector: 280 °C).

### 4.2. Preparation of (perfluorobutyl)-ethene

#### 4.2.1. Preparation of (perfluorobutyl)-ethene (*6a*) by the TBAF assisted cleavage of *3a*, *4a*, and *5a* (Table 1, entries1–3)

In a round bottomed flask equipped for distillation was placed the α-iodoethylsiloxane (**3a**, 4.39 g, 5.0 mmol), or the alkenylsiloxane (**4a**, 3.11 g, 5.0 mmol), or the alkenylfluorosilane (**5a**, 3.22 g, 10 mmol), $TBAF{\cdot}3H_2O$ (4.73 g, 15 mmol) and 10 mL of DMF, respectively. Then the mixture was stirred and heated at 100 °C with an oil bath. The evolution of the title olefin started immediately and the distillations were complete within 30 min. Yield: 2.19 g (89%/**3a**), or 1.85 g (75%/**4a**), or 1.80 g (73%/**5a**) colorless oils, all with GC assay: 98%. The NMR data were in agreement with those reported [4].

#### 4.2.2. Preparation of (perfluoroalkyl)-ethenes (*6a–c*) by the KF/NEt$_3$/H$_2$O assisted cleavage of *3a–c* in DMF (Table 1, entries 4–6)

In a round bottomed flask equipped for distillation was placed the α-iodoethylsiloxane (**3a**, 4.39 g, 5.0 mmol, or **3b**, 5.39 g, 5.0 mmol, or **3c**, 6.39 g, 5.0 mmol), KF (0.87 g, 15 mmol) $NEt_3$ (1.52 g, 15 mmol), $H_2O$ (0.27 g, 15 mmol) and 15 mL of DMF. Then the mixture was stirred and heated at 160 °C with an oil bath. The evolution of the title olefin started immediately and the distillations were complete within 30 min. The biphasic distillate was diluted with water and the lower phase was separated and co-distilled with pyridine. The distillate was washed with 5% HCl solution. The lower phase was separated and dried over $Na_2SO_4$. Yields: 1.65 g (67% of **6a**), or 2.42 g (70% of **6b**), or 3.70 g (83% of **6c**) colorless oils, all with GC assay: 98–99%. The NMR data were in agreement with those reported [4].

#### 4.2.3. Effect of the length of the fluorous chain on the coupling of β-perfluoroalkyl-a-iodoethyl-siloxanes (*3a–c*) with iodobenzene (cf. Scheme 5)

Under argon atmosphere in a round bottomed flask which is equipped with a reflux condenser a mixture of $(R_{fn}CH_2CHISiMe_2)_2O$ (3.38 g **3a**, or 4.15 g **3b** or 4.92 g **3c**, 3.85 mmol), $C_6H_5I$ (**7a**, 1.43 g, 7.0 mmol), $TBAF{\cdot}3H_2O$ (3.31 g, 10.5 mmol), $NEt_3$ (1.06 g, 10.5 mmol), $Pd(OAc)_2$ (31 mg, 2 mol%) and DMF (16 mL) were heated to 100 °C and stirred for 3 h. The product was isolated with steam-distillation. The distillate (50 mL) was extracted with ether (3 × 15 mL) and the combined organic layers were dried ($Na_2SO_4$), then the solvent was removed by evaporation (Rotavap). The crude product was purified with flash chromatography (50 mL *n*-hexane, 2.5 cm × 4 cm column, silica 60). Yield 1.40 g (62%/**3a**) of **8aa** = **8a** (GC: 95%), 1.66 g (56%/**3b**) of **8ba** (GC: 95%), and 2.12 g (58%/**3c**) of **8ca** (GC: 97%). The spectroscopic data of products were in agreement with those reported [15].

### 4.3. Tandem Heck-reactions with substituted iodobenzenes (General Procedure-1, GP-1)

Under argon atmosphere in a round bottomed flask which is equipped with a reflux condenser a mixture of $(R_{f4}CH_2CHISiMe_2)_2O$ (**3a**, 0.88 g, 1.0 mmol), iodoarene (**7a**–**i**, 0.7 mmol), KF (0.12 g, 2.1 mmol), $NEt_3$ (0.28 g, 2.8 mmol), $Pd(OAc)_2$ (3.1 mg, 0.014 mmol, 2 mol%) and DMF (1.5 mL) were heated to 120 °C and stirred for 5–14 h. The mixture was extracted with ether (2 × 15 mL) and the combined organic layers were dried ($Na_2SO_4$), then the solvent was removed by evaporation (Rotavap). The crude product was purified with flash chromatography (50 mL *n*-hexane, 2.5 cm × 4 cm column, silica 60).

#### 4.3.1. (E)-1-Methoxy-2-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (*8b*)

The reaction was performed according to GP-1 using 2-iodoanisole (**7b**) (0.164 g, 0.70 mmol) for 5 h. Yield: 0.210 g (85%), GC assay: 98%. $^1H$ NMR ($CDCl_3$): $\delta = 3.78$ (s, 3 H, $OCH_3$); 6.25

(dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, $CF_2$–CH); 6.60–7.40 (m; 5H, Ar–CH overlaps with aromatic protons). $^{13}$C NMR ($CDCl_3$): $\delta = 55.7$ (s, O*C*$H_3$), 111.4 (s, $C_{Ar}$), 114.9 (t, $^2J_{CF}$ = 23 Hz, $CF_2$–CH), 120.9 (s; $C_{Ar}$), 122.7 ($C_{Ar,ipso}$), 128.9 (s, $C_{Ar}$), 131.5 (s, $C_{Ar}$), 135.4 (t, $^3J_{CF}$ = 10 Hz, Ar–CH), 158.2 (s, $C_{Ar,\ ipso}$). $^{19}$F NMR ($CDCl_3$): $\delta = -81.55$ (t, $^3J_{FF}$ = 10.5 Hz, 3F), −112.12 (m; 2F), −124.60 (m; 2F), −126.20 (m; 2F). MS (EI, *m/z*) 183 (MeO–$C_6H_4$–CH=CH–$CF_2^+$), 163, 151, 133, 119 ($C_2F_5^+$), 91 ($C_8H_7$), 77 ($C_6H_5^+$), 69 ($CF_3^+$), 51 ($C_4H_3^+$).

### *4.3.2. (E)-1-Methoxy-3-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (**8c**)*

The reaction was performed according to GP-1 using 3-iodoanisole (**7c**) (0.164 g, 0.70 mmol), for 5 h. Yield: 0.163 g (66%), GC assay: 96%. The spectroscopic data were in agreement with those reported [15].

### *4.3.3. (E)-1-Methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (**8d**)*

The reaction was performed according to GP-1 using 4-iodoanisole (**7d**) (0.164 g, 0.70 mmol), for 5 h. Yield: 0.155 g (63%), GC assay: 95%. The spectroscopic data were in agreement with those reported [15].

### *4.3.4. (E)-1-Chloro-2-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (**8e**)*

The reaction was performed according to GP-1 using 2-chloroiodobenzene (**7e**) (0.167 g, 0.70 mmol), for 14 h. Yield: 0.175 g (70%), GC assay: 95%. $^1$H NMR ($CDCl_3$): $\delta = 6.51$ (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HF}$ = 12 Hz, 1H, $CF_2$–CH); 7.20–8.20 (m; 5H, Ar–CH overlaps with aromatic protons). $^{13}$C NMR ($CDCl_3$): $\delta = 117.2$ (t, $^2J_{CF}$ = 23 Hz, $CF_2$–CH), 127.4 (s; $C_{Ar}$), 128.1 (s, $C_{Ar}$), 129.6 (s, $C_{Ar}$), 130.3 (s; $C_{Ar}$), 131.3 (s; $C_{Ar}$), 134.7 (s, $C_{Ar}$), 136.5 (t, $^3J_{CF}$ = 10 Hz, Ar–CH). $^{19}$F NMR ($CDCl_3$): $\delta = -81.57$ (t, $^3J_{FF}$ = 10.5 Hz, 3F), −111.70 (m; 2F), −124.60 (m; 2F), −126.20 (m; 2F). MS (*m/z*): 187 and 189 (Cl–$C_6H_4$–CH=CH–$CF_2^+$; 2:1 intensity ratio due to Cl izotopes), 167 and 169 (2:1 intensity ratio due to Cl izotopes), 151, 133, 119 ($C_2F_5^+$), 77 ($C_6H_5^+$), 69 ($CF_3^+$), 51 ($C_4H_3^+$).

### *4.3.5. (E)-1-Methyl-2-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (**8f**)*

The reaction was performed according to GP-1 using 2-iodotoluene (**7f**) (0.153 g, 0.70 mmol), for 5 h. Yield: 0.220 g (93%), GC assay: 95%. The spectroscopic data were in agreement with those reported [15].

### *4.3.6. (E)-1-Methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (**8g**)*

The reaction was performed according to GP-1 using 4-iodotoluene (**7g**) (0.153 g, 0.70 mmol), for 8 h. Yield: 0.158 g (67%), GC assay: 95%. The spectroscopic data were in agreement with those reported [15].

### *4.3.7. (E)-1-Trifluoromethyl-3-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-benzene (**8h**)*

The reaction was performed according to GP-1 using 3-iodobenzotrifluoride (**7h**) (0.190 g, 0.70 mmol), for 11 h. Yield: 0.158 g (58%), GC assay: 95%. The spectroscopic data were in agreement with those reported [15].

### *4.3.8. (E)-1-(3,3,4,4,5,5,6,6,6-nonafluoro-hexen-1-yl)-naphtalene (**8i**)*

The reaction was performed according to GP-1 using 1-iodonaphtalene (**7i**) (0.178 g, 0.70 mmol), for 10 h. Yield: 0.195 g (75%) yellow oil. GC assay: 95%. The spectroscopic data were in agreement with those reported [15].

## *4.4. Preparation and use of a 'silica supported β-perfluoroalkyl-α-iodoethyl-trialkoxy-silane' (**11**)*

### *4.4.1. Synthesis of β-(n-perfluorooctyl)-α-iodoethyl-trimethoxy-silane (**10**)*

$C_8F_{17}I$ (24.5 g, 45 mmol) and $CH_2{=}CH{-}Si(OMe)_3$ (**9**, 5.04 g, 34 mmol) were placed into an oven dried round bottomed flask which was equipped with a reflux condenser and magnetic stirrer bar. The mixture was heated to 80 °C and azobisisobutyronitrile (AIBN, 0.9 g, 5.5 mmol) was introduced in small increments during 2.5 h. It was stirred an additional 3 h at 80 °C. The product was isolated by short-path distillation. Yield: 17.5 g (74%) of slightly violet liquid, which was collected at 140 °C bath temperature @ 0.10 mmHg pressure, GC assay: 92.5%.

$^1$H NMR ($CDCl_3$): $\delta = 2.45$–3.05 (m; 2H, $CH_2$); 3.10–3.20 (m; 1H, CHI), 3.65 (s, 9H, O$CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta = -11.2$ (s, *C*H), 34.7 (t, $^2J_{CF}$ = 21.5 Hz, *C*$H_2$), 52.26 (s, O*C*$H_3$). $^{19}$F NMR ($CDCl_3$): $\delta = -81.39$ (t; $^3J_{FF}$ = 10.5 Hz; 3F); −116.0 (m; 2F); −122.2 (m; 2F); −122.5 (m, 4F), −123.3 (m; 2F); −124.2 (m; 2F); −126.7 (m; 2F).

Microanalysis for $C_{13}H_{12}F_{17}O_3SiI$ = 694.19 g/mol; calculated I 18.28%; found I, 18.12%.

### *4.4.2. Immobilization of a fluorous-trimethoxysilane onto silica gel*

Silica-gel 60 (20.0 g), trimethoxysilane derivative (**10**, 13.2 g, 19 mmol) and toluene (100 mL) was placed in a round bottomed flask equipped with a reflux condenser, $CaCl_2$ drying tube and magnetic stirrer bar. The mixture was heated to 130 °C and stirred for 28 h. The product was filtered by suction and washed with acetone (100 mL) and *n*-hexane (100 mL) and dried on the air. The yield is 31.1 g (99%) of white free flowing powder with 0.60 mmol/g bonded silane. Microanalysis: calculated I, 7.77%; found I, 7.69%.

### *4.4.3. Coupling reaction of silica supported (perfluoroalkyl)-ethene surrogate **11** and iodobenzene*

Under argon atmosphere in a round bottomed flask which is equipped with a reflux condenser and magnetic stirrer bar a mixture of **6a** (1.43 g, 7.0 mmol), reagent **11** (16.7 g, 10 mmol fluorous-ethene equivalent), KF (1.16 g, 20 mmol), $NEt_3$ (3.0 g, 30 mmol), $Pd(OAc)_2$ (16 mg, 0.067 mmol, 1 mol%) and DMF (40 mL) was heated to 140 °C and stirred for 5 h. After the reaction completed, the mixture was filtered, then the filtrate was diluted with water (100 mL) and extracted with ether (3 × 30 mL). The combined organic layers were washed with water (3 × 30 mL) and dried ($Na_2SO_4$), then the solvent was removed by evaporation (Rotavap). The crude product was purified with flash chromatography (50 mL *n*-hexane, 2.5 cm × 4 cm column, silica 60). Yield: 1.72 g (47%) of **8ca** as a colorless oil, GC assay: 96%. The NMR data were in agreement with those reported [15].

## *4.5. Cross-coupling reaction of the olefin sources **3a**, **4a**, and **5a** with iodobenzene (**7a**) in the presence of TBAF/NEt$_3$, TBAF, or KF/NEt$_3$ reagents yielding ω-(perfluorobutyl)-styrene (**8a**)*

Under argon atmosphere in a round bottomed flask which is equipped with a reflux condenser a mixture of $(R_{f4}CH_2CHISiMe_2)_2O$ (**3a**, 0.97 g, 1.1 mmol), or $(R_{f4}CH{=}CHSiMe_2)_2O$ (**4a**, 0.68 g, 1.1 mmol), or $R_{f4}CH{=}CHSiMe_2F$ (**5a**, 0.71 g, 2.2 mmol), respectively, and $C_6H_5I$ (**7a**, 0.41 g, 2.0 mmol), and the activator/base [TBAF·3$H_2O$ (0.69 g, 2.2 mmol) and $NEt_3$ (0.30 g, 3.0 mmol) (Condition A), or TBAF·3$H_2O$ (0.69 g, 2.2 mmol) (Condition B), or KF (0.13 g, 2.2 mmol) and 0.61 g (6.0 mmol) $NEt_3$, (Condition C) respectively], $Pd(OAc)_2$ (9 mg, 2 mol%) and DMF (5 mL) was heated to 100 °C and stirred for 1.5 h. Then the product was isolated with steam-distillation. The distillate (50 mL) was extracted with ether (3 × 15 mL) and the combined organic layers were dried ($Na_2SO_4$), then the solvent was removed by evaporation (Rotavap). The crude product was purified with flash chromatography (50 mL *n*-hexane, 2.5 cm × 4 cm column, silica 60).

*Condition A:* yields: 0.30 g (47%/**3a**), or 0.30 g (47%/**4a**), or 0.20 g (31%/**5a**) of colorless oils (with $NEt_3$/TBAF).

*Condition B:* yields: 0.00 g (0%/**3a**), or 0.25 g (39%/**4a**), or 0.20 g (31%/**5a**) of colorless oils (with TBAF).

*Condition C:* yields: 0.30 g (47%/**3a**), or 0.30 g (47%/**4a**), or 0.26 g (40%/**5a**) of colorless oils (KF/$NEt_3$). The NMR data for product **8a** were in agreement with those reported [15].

## Acknowledgements

These investigations were supported by the Hungarian Scientific Research Foundation (OTKA K062191 "Sustainable fluorous chemistry"). The European Union and the European Social Fund have provided financial support to the project under the grant agreement no. TÁMOP_4.2.1./B-09/1/KMR-2010-0003. Ágnes Csapó thanks the 'Sanofi-Aventis/Chinoin' for a PhD fellowship. We thank Szilárd Nász and Áron Kramarics for analytical assistance.

## References

[1] (a) T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, 3rd ed., Wiley, New York, 1991;
(b) P.J. Kocienski, Protecting Groups, 3rd ed., Georg Thieme Verlag, New York, 2005.

[2] (a) For use of KF*$2H_2O$ in methanol at 50 °C, see: A.G. Myers, P.M. Harrington, E.Y. Kuo, Journal of the American Chemical Society, 113 (1991) 694–695;
(b) For the use of TBAF/THF, see: A.G. Myers, S.D. Goldberg, Angewandte Chemie International Edition, 39 (2000) 2732–2735.

[3] Q.-Y. Chen, Z.-Y. Yang, D.-Q. Rang, Journal of Fluorine Chemistry 29 (1985) 147.

[4] Z. Szlávik, G. Tárkányi, Á. Gömöri, J. Rábai, Organic Letters 2 (2000) 2347–2349.

[5] (a) For a definition and recent advances of the Heck coupling, see: http://www.organic-chemistry.org/namedreactions/heck-reaction.shtm.
(b) J.-E. Bäckvall, Scientific Background on the Nobel Prize in Chemistry 2010: Palladium-Catalyzed Cross couplings in Organic Synthesis, The Royal Swedish Academy of Sciences, 2010 pp. 1–12 http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2010/Sciback_2010.pdf.

[6] (a) R.F. Heck, Accounts of Chemical Research 12 (1979) 146–151;
(b) R.F. Heck, Organic Reactions 27 (1982) 345–390.

[7] For the evolution of metal-catalyzed organic synthesis, see: N. Miyaura, Advanced Synthesis and Catalysis, 346 (2004) 1522–1523.

[8] (a) I.T. Horváth, J. Rábai, Science 266 (1994) 72–75;
(b) E.G. Hope, A.M. Stuart, Journal of Fluorine Chemistry 100 (1999) 75–83;
(c) J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley-VCH, Weinheim, 2004;
(d) For changing designers issues in fluorous chemistry, see: A.E.C. Collis, I.T. Horváth, Catalysis Science and Technology, 1 (2011) 912–919;
(e) X. Zhao, W.Y. Ng, K.-C. Lau, A.E.C. Collis, I.T. Horváth, Physical Chemistry Chemical Physics 14 (2012) 3909–3914.

[9] (a) W. Chen, L. Xu, J. Xiao, Tetrahedron Letters 42 (2001) 4275–4278;
(b) W. Chen, L. Xu, J. Xiao, Organic Letters 2 (2000) 2675–2677.

[10] (a) J. Salabert, R.M. Sebastián, A. Vallribera, A. Roglans, C. Nájera, Tetrahedron 67 (2011) 8659–8664;
(b) S. Darses, M. Pucheault, J.-P. Genêt, European Journal of Organic Chemistry 6 (2001) 1121–1128;
(c) K. Kikukawa, T. Matsuda, Chemistry Letters (1977) 159–162.

[11] (a) N.O. Brace, US Patent 3,016,406 (E. I. du Pont de Nemours and Company), January 9, 1962 (application: September 21, 1960); Chem. Abstr. (1962) 57, 2078a.;
(b) W. Boechl, Neth. Appl. 6,506,069. 1965 November 15 (application: May 14, 1964); Chem. Abstr. (1966), 64, 17421c.

[12] N.O. Brace, L.W. Marshall, C.J. Pinson, G. van Wingerden, Journal of Organic Chemistry 49 (1984) 2361–2368.

[13] P.M. Murphy, C.S. Baldwin, R.C. Buck, Journal of Fluorine Chemistry 138 (2012) 3–23.

[14] J. Rábai, in: J.A. Gladysz, D.P. Curran, I.T. Horvath (Eds.), Handbook of Fluorous Chemistry, Wiley-VCH, Weinheim, 2004, pp. 156–174 (Chapter 9).

[15] Á. Csapó, A. Bodor, J. Rábai, Journal of Fluorine Chemistry 137 (2012) 85–92.

[16] C. Szijjártó, P. Ivanko, F.T. Takács, D. Szabó, J. Rábai, Journal of Fluorine Chemistry 129 (2008) 386–389.

[17] D.P. Curran, Angewandte Chemie International Edition 37 (1998) 1174–1196.

[18] (a) D.P. Curran, S. Hadida, M. He, Journal of Organic Chemistry 62 (1997) 6714–6715;
(b) D.P. Curran, Synlett (2001) 1488–1496;
(c) W. Zhang, D.P. Curran, Tetrahedron 62 (2006) 11837–11865.

[19] For a method of preparing 1H,1H,2H,2H-perfluoroalkyltrialkoxysilane, see: G. Zhao, C. Bo, J. Lu, K. Li, Z. Gong, Faming Zhuanli Shenqing (2010), CN 101701023 A 20100505 (Chinese Patent).

[20] (a) R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, S. Niembro, F. Petrucci, R. Pleixats, A. Prastaro, R.M. Sebastián, R. Soler, M. Tristany, A. Vallribera, Organic Letters 10 (2008) 561–564;
(b) K. Hamza, R. Abu-Reziq, D. Avnir, J. Blum, Organic Letters 6 (2004) 925–927;
(c) A. Dahan, M. Portnoy, Organic Letters 5 (2003) 1197–1200;
(d) H. Hagiwara, Y. Sugawara, K. Isobe, T. Hoshi, T. Suzuki, Organic Letters 6 (2004) 2325–2328.