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On the reactions of trifluorovinylsilanes with aromatic ketones – Expected and some unexpected results

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Dedicated to the memory of
Prof. Dr. Lev Moiseevich Yagupolskii.

ABSTRACT

The reactions of aromatic ketones with trialkyl(trifluorovinyl)silanes in the presence of fluoride ions were studied. The conditions for the selective addition of trialkyl(trifluorovinyl)silanes to the carbonyl function of aromatic ketones in the presence of cesium fluoride and absence of any solvents to form the trifluorovinyl containing "silylated" alcohols have been worked out. The analogous reactions in common organic solvents are not terminated on the stage of "silylated" alcohols formation; consecutive reactions lead to fluorinated olefins and acids under the influence of fluoride ions.

1. Introduction

Trifluoroallylic alcohols are of great interest as synthons in fluoroorganic chemistry [1]. However, the possibilities to use them are strictly limited due to the absence of convenient synthetic methods. Up to now, there is mentioned only one method in the literature for the introduction of a trifluorovinyl group into aliphatic ketones by the reaction with trifluorovinyllithium [2–4]. For aromatic ketones, the reaction of acetophenone with trifluorovinyllithium yielding the trifluorovinyl containing alcohol is twice reported [4,5]. It should be noted that the stability of trifluorovinyllithium, even at low temperature, significantly limits the applicability of this method. It should also be mentioned that 1,2-bis(trimethylsilyl)-1,1,2,2-tetrafluoroethane has been used as a reagent to convert benzaldehyde and acetophenone into the appropriate trifluorovinyl alcohols [6]. Therefore, the search for available and shelf-stable reagents serving as trifluorovinyl group sources is of current interest. Previously, we showed that aromatic aldehydes react with trialkyl(trifluorovinyl)silanes in the presence of fluoride ions to form "silylated" trifluoroallylic alcohols. Furthermore, on the basis of the isolated products, we proposed a reaction scheme for the transformation of "silylated" alcohols under the influence of nucleophilic agents and Brönsted acids [7].

In the present paper, we report a new method to obtain "silylated" trifluoroallylic alcohols starting from aromatic ketones and trifluorovinylsilanes in the presence of fluoride ions, and their consecutive conversions into fluorinated olefins and acids.

2. Results and discussion

Previously, we elaborated the conditions for the reactions of aromatic aldehydes with trialkyl(trifluorovinyl)silanes ($Alk_3SiCF{=}CF_2$) in the presence of cesium fluoride (CsF) in dimethoxyethane (DME) or tetramethylammonium fluoride ($[Me_4N]F$) in diethyl ether giving trifluorovinyl containing "silylated" alcohols in high yields [7]. To complete our study, we investigated the reactions of aromatic ketones, namely 2,2,2-trifluoroacetophenone **1**, benzophenone **2** and acetophenone **3**, with trialkyl(trifluorovinyl)silanes in the presence of fluoride ions. However, we failed to synthesize trifluorovinyl containing "silylated" alcohols starting from aromatic ketones under the conditions optimized for aromatic aldehydes as mentioned above [7].

The reaction of equimolar amounts of 2,2,2-trifluoroacetophenone **1** and triethyl(trifluorovinyl)silane in the presence of CsF in DME or THF in the temperature range from −60 °C to room

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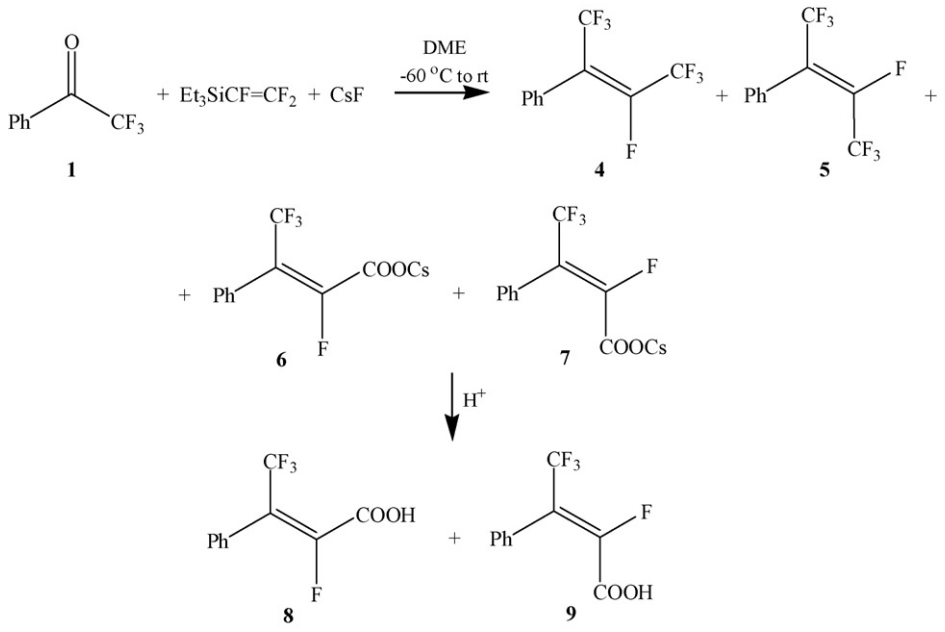


Scheme 1.

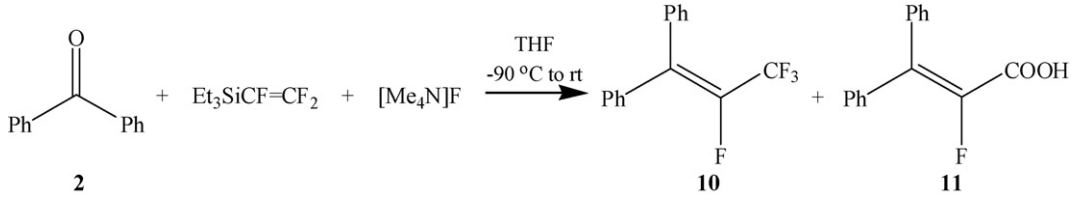
temperature results in the formation of *E*/*Z*-1,1,1,3,4,4,4-heptafluor-2-phenyl-but-2-enes **4**, **5** [8,9] and cesium salts of *E*/*Z*-2,4,4,4-tetrafluor-3-phenyl-but-2-enoic acids **6**, **7** instead of the expected "silylated" alcohol (Scheme 1). Salts **6**, **7** can be converted into the corresponding acids **8**, **9** by acidification.

It should be noted that solely aforesaid products are formed and not the expected "silylated" alcohols irrespective of reagents' ratio, the fluoride ion source, the solvent and the reaction temperature. The yield of the olefins **4** and **5** due to their high volatility was determined on the basis of ^{19}F NMR spectroscopic data relatively to fluorobenzene (C_6H_5F) which was used as an internal standard.

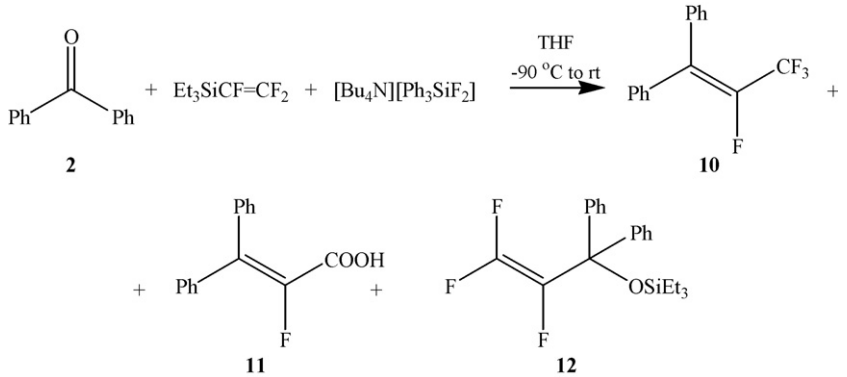
The reaction of benzophenone **2** with triethyl(trifluorovinyl)silane and tetramethylammonium fluoride ([Me_4N]F) (molar ratio 1:1:2) in tetrahydrofurane (THF) in the temperature range from −90 °C to 20 °C leads to the formation of 2,3,3,3-tetrafluoro-1,1-diphenyl-prop-1-ene **10** [10] in 51% yield; 2-fluoro-3,3-diphenyl-acrylic acid **11** [3,11] is obtained after acidification of the corresponding tetramethylammonium salt in 41% yield (Scheme 2).

The use of tetrabutylammonium triphenyldifluorosilicate ([NBu_4][Ph_3SiF_2]) as a fluoride ion source allowed to detect (^{19}F NMR) the formation of ≈15% of the "silyl ether" **12** among the other products (Scheme 3).

This observation may serve as a confirmation of the reaction scheme we proposed previously for the interaction of aromatic aldehydes with trifluorovinylsilane in the presence of fluoride ions leading to the initial formation of "silylated" alcohols and their further conversions to the corresponding olefins and acids under the influence of fluoride ions [7] (Scheme 4).



Scheme 2.



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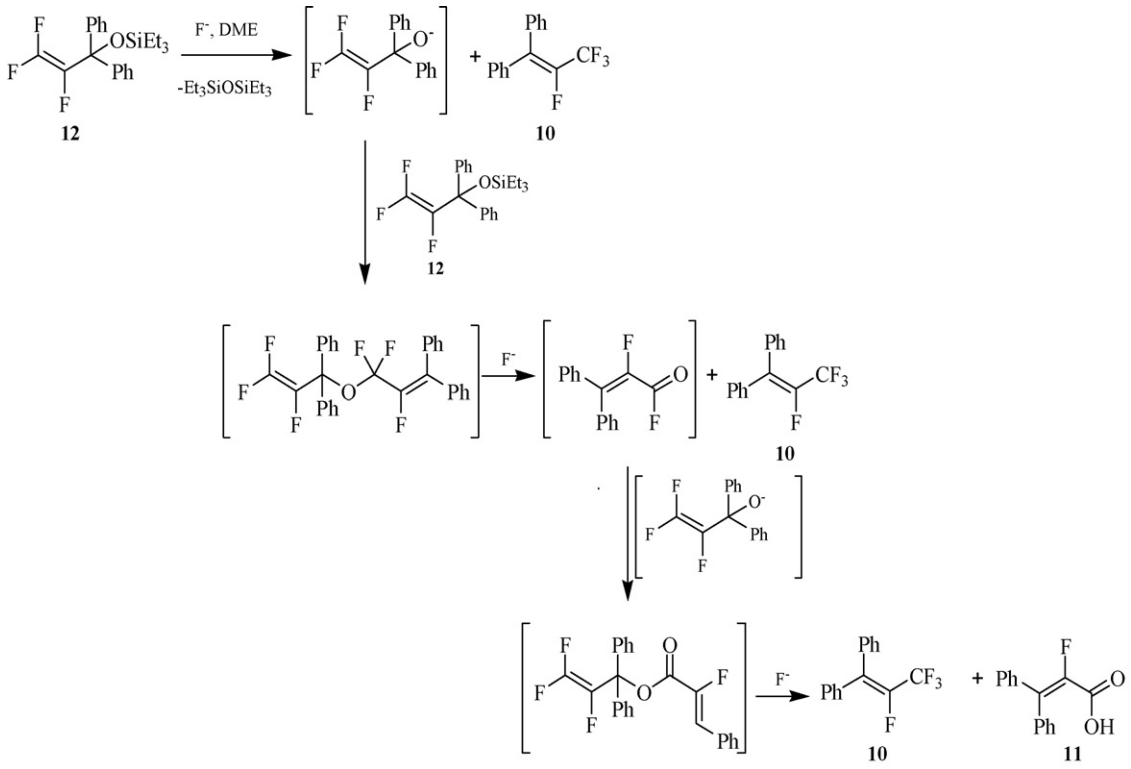


Scheme 4.

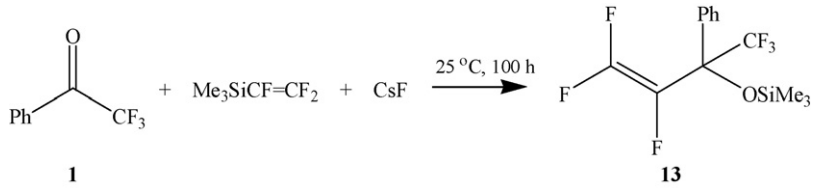
Most probably, tertiary trifluorovinyl containing "silylated" alcohols are more reactive in comparison to their secondary analogues and – under these reaction conditions – immediately undergo consecutive reactions with fluoride ions once being formed, thus preventing their isolation.

It should be noted that the fluorinated olefins and acids obtained in the course of research are of practical interest, but traditional methods to obtain them hamper from that they are frequently multi-step and based on commercially unavailable substrates. Taking into consideration the availability of the reagents we have used together with good yields of the final products, the present method may be proposed as an alternative route to obtain fluorinated olefins and acids.

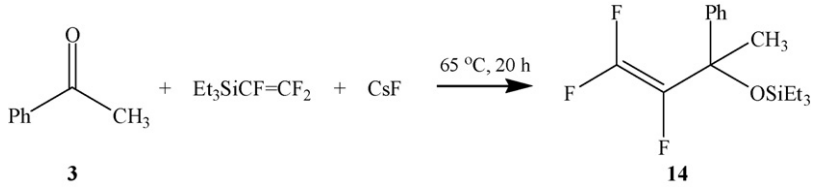
It is known that in some cases that performing reactions without any solvent significantly influence the conversion procedures and the product formation. As a consequence, our further attempts were directed towards the exploration of the reaction of aromatic ketones with trifluorovinylsilanes and fluoride ions in absence of any solvent.

We found that 2,2,2-trifluoroacetophenone **1** reacts with trimethyl(trifluorovinyl)silane in the presence of a 20% amount of CsF at 25 °C during 100 h to give 1,1,1,3,4,4-hexafluoro-1-trimethylsiloxy-1-phenyl-but-3-ene **13**. The degree of conversion of 2,2,2-trifluoroacetophenone gains 95% with the main product content in the mixture being 80% (Scheme 5). The "silylated" alcohol **13** was isolated using column chromatography and was fully characterized.

Using a molar amount of cesium fluoride and rise of the reaction temperature caused lower amounts of the "silylated" alcohol **13** but a concurrent increase of the formation of the fluorinated olefins **4**, **5** and the salts **6**, **7**. By the way, triethyl(trifluorovinyl)silane does not react under the chosen conditions; a fact which supports our



Scheme 5.



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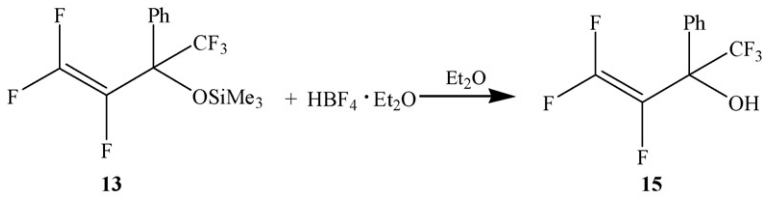
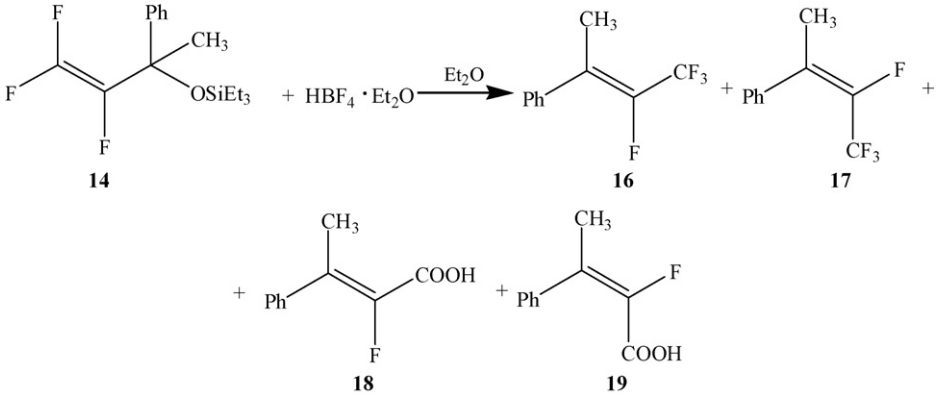


Scheme 7.



Scheme 8.

previously stated suggestion about significant differences between the reactivity of triethyl- and trimethyl(trifluorovinyl)silanes [7].

The reaction of acetophenone **3** with triethyl(trifluorovinyl)silane in the presence of cesium fluoride in the molar ration 1:1.2:1 at 65 °C during 20 h leads to the selective formation of 3,4,4-trifluoro-1-triethylsiloxy-1-phenyl-but-3-ene **14** (Scheme 6).

The degree of conversion of acetophenone **3** in the above reaction does not exceed 80% even if an excess of the silane is used. It should be also mentioned that using the more reactive trimethyl(trifluorovinyl)silane in this reaction as well as a decrease of the amount of cesium fluoride significantly lowers the degree of conversion of the starting substrate **3**.

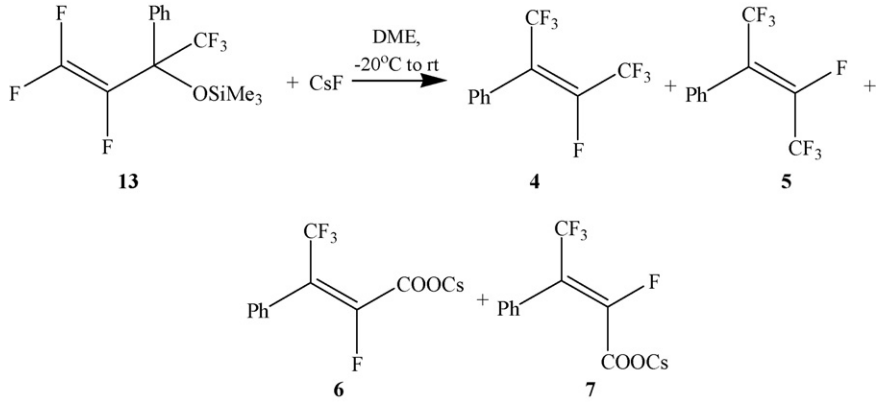
The desilylation to form "free" alcohols proceeds under the action either of acids or bases. Among the acids tested for acidification, the $HBF_4{\cdot}Et_2O$ complex became the reagent of choice making it possible to proceed the reaction under anhydrous conditions. The "silylated" alcohol **13** reacts with $HBF_4{\cdot}Et_2O$ in diethyl ether at room temperature selectively to form the 1,1,1,3,4,4-hexafluoro-2-phenyl-but-3-en-2-ol **15** (Scheme 7) which was monitored by ^{19}F NMR spectroscopic means. Compound **15** was isolated and fully characterized.

In contrast to 2,2,2-trifluoroacetophenone **1**, the reaction of "silylated" alcohol **14** with $HBF_4{\cdot}Et_2O$ under similar conditions is not terminated on the step of the "free" alcohol; consecutive reaction leads to fluorinated olefins **16**, **17** and acids **18**, **19** (Scheme 8). The course of the reaction was monitored by ^{19}F NMR spectroscopy. Spectral data of **16**, **17** [5] and **18**, **19** [4] correspond with literature data.

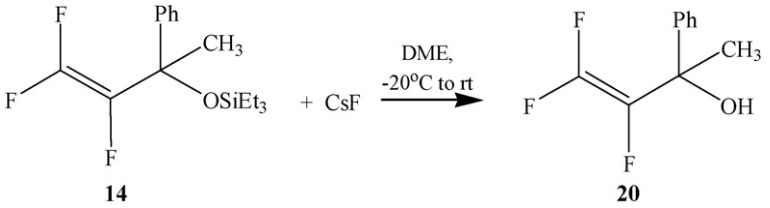
CsF being widely used in analogous reactions was chosen as a base. It was found out that the "silylated" alcohol **13** reacts with CsF in molar ratio 1:1 in DME in the temperature range from −20 °C to 20 °C to form the expected mixture of the products of its consecutive conversions, i.e. *E*/*Z*-1,1,1,3,4,4,4-heptafluor-2-phenylbut-2-enes **4**, **5** in a ratio 9:1 and cesium salts of *E*/*Z*-2,4,4,4-tetrafluor-3-phenylbut-2-enoic acids **6**, **7** in a 4:1 ratio (Scheme 9).

The reaction of the "silylated" alcohol **14** with CsF under similar conditions leads to the selective formation (^{19}F NMR control) of 3,4,4-trifluoro-2-phenyl-but-3-en-2-ol **20** [4,5] (Scheme 10).

It should be noted that our attempts to synthesize the trifluorovinyl containing "silylated" alcohol starting from benzophenone **2** and trialkyl(trifluorovinyl)silanes in the presence of fluoride ion without a solvent remained unsuccessful.



Scheme 9.



14 20

Scheme 10.

3. Conclusions

On the basis of the results reported, it can be concluded that aromatic ketones react with trialkyl(trifluorovinyl)silanes in the presence of fluoride ions without a solvent to form tertiary trifluorovinyl containing "silylated" alcohols that can be easily converted into the corresponding alcohols. The analogous reactions in common organic solvents are not terminated on the stage of "silylated" alcohols formation but proceed with consecutive reactions to fluorinated olefins and acids. Such fluorinated products are of practical interest but are limited by the lack of commercially available starting materials. The method proposed enables a one-step synthesis of a set of fluorinated olefins and acids starting from available organic substrates and is, therefore, highly perspective.

4. Experimental

All reactions were carried out under a dry argon atmosphere by using Schlenk techniques. The following products were synthesized according to literature procedures: $Me_3SiCF{=}CF_2$ [12], $Et_3SiCF{=}CF_2$ [12], $[Me_4N]F$ [13]. Aromatic ketones were purchased from Acros, $HBF_4{\cdot}Et_2O$ from Fluka. All solvents were purified according to literature procedures [14]. NMR spectra were recorded with the Bruker spectrometers AC 200, Avance 400, Avance DRX 500 and the Varian spectrometer VXR-300. Chemical shifts are given in ppm relative to Me_4Si (^1H, ^{13}C) and CCl_3F (^{19}F) as external standards. Melting points were measured in one-end open glass capillaries and are uncorrected. Column chromatography was carried out using 60–240 mesh silica gel at atmospheric pressure. CHNF-analyses were performed with the apparatus HEKAtech Euro EA 3000 and Analytikjena Spekol 1100.

4.1. Preparation of 2,3,3,3-tetrafluoro-1,1-diphenyl-prop-1-ene 10 and 2-fluoro-3,3-diphenyl-acrylic acid 11

To the solution of $Et_3SiCF{=}CF_2$ (1.08 g, 5.5 mmol) in tetrahydrofuran (THF) (50 mL) at −90 °C $[Me_4N]F$ (0.93 g, 10 mmol) was added. The mixture was stirred for 0.5 h at −85 ± 5 °C and then benzophenone **2** (0.91 g, 5 mmol) was added at −70 °C. The reaction mixture was allowed to warm to room temperature over 4 h. The precipitate formed (tetramethylammonium salt of 2-fluoro-3,3-diphenyl-acrylic acid) was filtered, washed with 5% aqueous HCl (5 mL), and water (2× 5 mL), then dissolved in 20% aqueous NaOH (10 mL). Insoluble impurities were filtered off, and the filtrate was acidified with 5% aqueous HCl to the isotonic point. The precipitate formed was filtered, dried and yielded 0.48 g (40%) of 2-fluoro-3,3-diphenyl-acrylic acid **11**. Physical and spectral characteristics of **11** correspond to literature data [3,11].

THF and volatile products were evaporated in vacuum, and hexane was added to the residue. Insoluble impurities were filtered off, and hexane was evaporated in vacuum. The residue was purified by silica gel column chromatography, yielded 0.68 g (51%) of 2,3,3,3-tetrafluoro-1,1-diphenyl-prop-1-ene **10**. Physical and spectral characteristics of **10** correspond to literature data [10].

4.2. Preparation of 1,1,1,3,4,4-hexafluoro-1-trimethylsiloxy-1-phenyl-but-3-ene 13

A mixture of 2,2,2-trifluoroacetophenone **1** (0.87 g, 5 mmol), $Me_3SiCF{=}CF_2$ (1.16 g, 7.5 mmol) and CsF (0.15 g, 1 mmol) was stirred for 100 h at 26 ± 1 °C, and then diethyl ether was added. Insoluble impurities were filtered off, and diethyl ether and volatile products were evaporated in vacuum. The residue was purified by silica gel column chromatography, yielded 1.05 g (64%) of 1,1,1,3,4,4-hexafluoro-1-trimethylsiloxy-1-phenyl-but-3-ene **13**. ^1H NMR spectral data (500.13 MHz, $CDCl_3$): δ 0.21 (s, 3H, CH_3), 7.44 (m, 3H, Ph), 7.63 (m, 2H, Ph). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 0.90 (s, CH_3), 78.51 (m, C_q), 123.34 (q, J = 287 Hz, CF_3), 127.01 (s, C_{Ph}), 128.37 (s, C_{Ph}), 128.17 (ddd, J = 241 Hz, J = 41 Hz, J = 19 Hz, CF), 129.51 (s, C_{Ph}), 134.75 (d, J = 1.6 Hz, C_{Ph}), 154.39 (ddd, J = 335 Hz, J = 289 Hz, J = 45 Hz, CF_2). ^{19}F NMR (188.14 MHz, $CDCl_3$): δ −78.13 (dd, 3F, J = 12 Hz, J = 10 Hz, CF_3), −98.74 (dd, 1F, J = 65 Hz, J = 36 Hz, CF), −108.42 (ddq, 1F, J = 116 Hz, J = 65 Hz, J = 12 Hz, CF), −177.89 (ddd, 1F, J = 116 Hz, J = 36 Hz, J = 10 Hz, CF). Anal. Calcd for $C_{13}H_{14}F_6OSi$: C, 47.57; H, 4.30; F, 34.73. Found: C, 47.69; H, 4.36; F, 34.84.

4.3. Preparation of 3,4,4-trifluoro-1-triethylsiloxy-1-phenyl-but-3-ene 14

A mixture of acetophenone **3** (0.60 g, 5 mmol), $Et_3SiCF{=}CF_2$ (1.18 g, 6 mmol) and CsF (0.76 g, 5 mmol) was stirred for 20 h at 65 ± 1 °C, and then hexane was added. Insoluble impurities were filtered off, and hexane and volatile products were evaporated in vacuum. The residue was purified by silica gel column chromatography, yielded 0.81 g (51%) of 3,4,4-trifluoro-1-triethylsiloxy-1-phenyl-but-3-ene **14**. ^1H NMR spectral data (500.13 MHz, $CDCl_3$): δ 0.69 (q, 2H, J = 8 Hz, CH_2), 1.01 (t, 3H, J = 8 Hz, CH_3), 1.76 (dd, 3H, J = 5 Hz, J = 2 Hz, CH_3), 7.30 (m, 1H, Ph), 7.37 (m, 2H, Ph), 7.48 (m, 2H, Ph). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 6.14 (s, CH_2), 6.84 (s, CH_3), 74.83 (ddd, J = 23 Hz, J = 4 Hz, J = 1.3 Hz, C_q), 125.05 (s, C_{Ph}), 127.48 (s, C_{Ph}), 128.17 (s, C_{Ph}), 132.48 (ddd, J = 239 Hz, J = 43 Hz, J = 15 Hz, CF), 144.86 (s, C_{Ph}), 153.3 (ddd, J = 330 Hz, J = 282 Hz, J = 48 Hz, CF_2). ^{19}F NMR (188.14 MHz, $CDCl_3$): δ −101.22 (dd, 1F, J = 78 Hz, J = 34 Hz, CF), −112.51 (ddq, 1F, J = 113 Hz, J = 78 Hz, J = 5 Hz, CF), −177.89 (ddd, 1F, J = 113 Hz, J = 34 Hz, J = 2 Hz, CF). Anal. Calcd for $C_{16}H_{23}F_3OSi$: C, 60.73; H, 7.33; F, 18.01. Found: C, 60.51; H, 7.26; F, 17.94.

4.4. Preparation of 1,1,1,3,4,4-hexafluoro-2-phenyl-but-3-en-2-ol 15

To the solution of 1,1,1,3,4,4-hexafluoro-1-trimethylsiloxy-1-phenyl-but-3-ene **13** (0.98 g, 3 mmol) in diethyl ether (5 mL) $HBF_4{\cdot}Et_2O$ (5 g, 31 mmol) was added. The mixture was stirred at 20 °C until the reaction was completed (monitored by ^{19}F NMR spectroscopy). To the solution were added diethyl ether (10 mL), water (20 mL) and $NaHCO_3$ to neutralize HBF_4. The product was extracted with diethyl ether (2× 10 mL). The combined ether phases were washed with water (10 mL), dried ($MgSO_4$) and concentrated in vacuum to yield 0.66 g (86%) of 1,1,1,3,4,4-hexafluoro-2-phenyl-but-3-en-2-ol **15**. ^1H NMR spectral data (299.94 MHz, $CDCl_3$): δ 3.54 (s, 1H, OH), 7.44–7.48 (m, 3H, Ph),

7.64–7.67 (m, 2H, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 76.42 (m, C_q), 123.95 (q, J = 288 Hz, CF_3), 126.94 (s, C_{Ph}), 129.01 (s, C_{Ph}), 128.17 (ddd, J = 241 Hz, J = 40 Hz, J = 20 Hz, CF), 130.24 (s, C_{Ph}), 133.59 (s, C_{Ph}), 154.97 (ddd, J = 333 Hz, J = 287 Hz, J = 46 Hz, CF_2). ^{19}F NMR (188.14 MHz, $CDCl_3$): δ −76.89 (t, 3F, J = J = 9 Hz, CF_3), −95.96 (dd, 1F, J = 65 Hz, J = 37 Hz, CF), −107.98 (ddq, 1F, J = 117 Hz, J = 65 Hz, J = 9 Hz, CF), −178.54 (ddd, 1F, J = 117 Hz, J = 37 Hz, J = 9 Hz, CF). Anal. Calcd for $C_{10}H_6F_6O$: C, 47.89; H, 2.36; F, 44.51. Found: C, 47.69; H, 2.29; F, 44.37.

4.5. Preparation of *E*-1,1,1,3,4,4,4-heptafluor-2-phenylbut-2-ene 4, *Z*-1,1,1,3,4,4,4-heptafluor-2-phenylbut-2-ene 5, *E*/*Z*-2,4,4,4-tetrafluoro-3-phenyl-but-2-enoic acids 8, 9

Method A: To a mixture of 2,2,2-trifluoroacetophenone **1** (0.87 g, 5 mmol) and $Et_3SiCF{=}CF_2$ (1.13 g, 5.75 mmol) in dimethoxyethane (DME) (50 mL) at −60 °C CsF (0.76 g, 5 mmol) was added. The mixture was stirred for 1 h at −35 ± 5 °C and then overnight at room temperature. The yield of olefines **4** (0.35 g, 27%) and **5** (0.08 g, 6%) was determined by ^{19}F NMR experiments (relative to fluorobenzene (C_6H_5F)). Spectral characteristics of **4** and **5** correspond to literature data [8,9]. All volatile products and DME were evaporated in vacuum, and hexane (10 mL) was added to the residue. The precipitate formed, was filtered, washed with hexane and dried to give the products **6**, **7** (cesium salts of *E*/*Z*-2,4,4,4-tetrafluoro-3-phenyl-but-2-enoic acids, 0.70 g, 38%). Salts **6**, **7** were dissolved in water (15 mL), insoluble impurities were extracted with diethyl ether (2× 7 mL), then water phase was acidified with 5% aqueous HCl to the isotonic point. The oil formed after acidification was extracted with ethylacetate, dried ($MgSO_4$), concentrated in vacuum and yielded 0.41 g (35%) of *E*/*Z*-2,4,4,4-tetrafluoro-3-phenyl-but-2-enoic acids **8**, **9** (*E*/*Z* = 4:1). (*E*) Isomer: ^{1}H NMR spectral data (299.94 MHz, $CDCl_3$): δ 7.31–7.50 (m, 5 H, Ph). ^{13}C NMR (100.62 MHz, $(CD_3)_2SO$): δ 120.13 (qd, J = 31.5 Hz, J = 8.6 Hz, C=), 123.33 (q, J = 275 Hz, CF_3), 128.32 (s, C_{Ph}), 129.42 (s, C_{Ph}), 130.38 (s, C_{Ph}), 130.58 (d, J = 2.9 Hz, C_{Ph}), 151.74 (d, J = 282 Hz, CF=), 160.73 (d, J = 34 Hz, COOH). ^{19}F (188.14 MHz, $CDCl_3$): δ −59.39 (d, 3F, J = 24 Hz, CF_3), −106.71 (q, 1F, J = 24 Hz, CF). (*Z*) Isomer: ^{1}H NMR spectral data (299.94 MHz, $CDCl_3$): δ 7.31–7.50 (m, 5H, Ph). ^{13}C NMR (100.62 MHz, $(CD_3)_2SO$): δ 117.94 (qd, J = 33.5 Hz, J = 10.8 Hz, C=), 123.49 (q, J = 272 Hz, CF_3), 129.91 (s, C_{Ph}), 130.17 (d, J = 1.5 Hz, C_{Ph}), 130.73 (s, C_{Ph}), 153.83 (d, J = 274 Hz, CF=), 161.30 (d, J = 34 Hz, COOH). ^{19}F (188.14 MHz, $CDCl_3$): δ −57.54 (d, 3F, J = 10 Hz, CF_3), −104.48 (q, 1F, J = 10 Hz, CF).

Method B: To the solution of 1,1,1,3,4,4-hexafluoro-1-trimethylsiloxy-1-phenyl-but-3-ene **13** (0.98 g, 3 mmol) in DME (30 mL) at −20 °C CsF (0.46 g, 3 mmol) was added. The mixture was stirred for 1 h at −20 °C and then overnight at room temperature. The precipitate formed was filtered off, the filtrate was concentrated, and the residue was dissolved in water. The water phase was acidified with 5% aqueous HCl to the isotonic point, the oil formed after acidification was extracted with ethylacetate, dried ($MgSO_4$), concentrated in vacuum and yielded 0.39 g (55%) of *E*/*Z*-2,4,4,4-tetrafluoro-3-phenyl-but-2-enoic acids **8**, **9** (*E*/*Z* = 4:1).

4.6. Preparation of 3,4,4-trifluoro-2-phenyl-but-3-en-2-ol 20

To the solution of 3,4,4-trifluoro-1-triethylsiloxy-1-phenyl-but-3-ene **14** (0.63 g, 2 mmol) in DME (15 mL) at −20 °C CsF (0.46 g, 3 mmol) was added. The mixture was stirred for 1 h at −20 °C and then overnight at room temperature until the reaction was completed (monitored by ^{19}F NMR spectroscopy). The yield of 3,4,4-trifluoro-2-phenyl-but-3-en-2-ol **20** (0.36 g, 90%) was determined by ^{19}F NMR experiments (relative to fluorobenzene (C_6H_5F)). Spectral characteristics of **20** correspond to literature data [4].

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