Tetrahedron 66 (2010) 1832–1836

Contents lists available at ScienceDirect

Tetrahedron

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

Elaboration of a Lewis acid-free protocol for the alkylation of silicon-containing π-donors by β-arylthioalkyl chlorides

Maxim O. Ratnikov [a,*], Vasily V. Tumanov [b], William A. Smit [b]

[a] Department of Chemistry and Biochemistry, 0107 Chemistry Building, University of Maryland, College Park, MD 20742, USA
[b] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp., 47, Moscow 119991, Russian Federation

ARTICLE INFO

Article history:
Received 23 November 2009
Received in revised form 21 December 2009
Accepted 8 January 2010
Available online 18 January 2010

Keywords:
Electrophilic addition
Trifluoroethanol
Hexafluoroisopropanol
Hydrogen bonds

ABSTRACT

Hexafluoroisopropanol (HFIP) was found to be a powerful electrophilic activator of covalent reagents. Due to this effect the title reaction was shown to proceed under mild conditions in the absence of any Lewis acid catalysts to give the respective products of C-alkylation in good to excellent yields.

© 2010 Elsevier Ltd. All rights reserved.

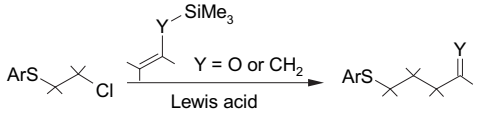
1. Introduction

Polyfluorinated alcohols such as trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP) are known as solvents with a unique set of properties.[1] Due to the presence of electron withdrawing trifluoromethyl group(s) these compounds exhibit the properties of highly polar solvents[2] with extremely high ionizing power,[3] very low nucleophilicity,[4] and the ability to serve as powerful hydrogen-bond donors toward both neutral and charged nucleophiles.[5]

These properties of TFE and HFIP allowed their successful applications as the media to perform such transformations as solvolysis,[6] nucleophilic opening of oxiranes,[7] intramolecular electrophilic addition to C=C bonds,[8] and aromatic electrophilic substitution[4a,9] in the absence of any other activating agents. Recently we have shown that HFIP could be employed as a medium and an activator for a number of classical C–C bond forming reactions of carbonyl compounds and their acetals such as Hosomi–Sakurai acetal allylation, Mykaiyama aldol reaction, and Sakurai–Mukaiyama conjugate additions that could be carried out in this solvent without any catalysts under rather mild conditions.[10] Here we present the results of our preceding studies, which had been aimed at the elaboration of this novel electrophile activation methodology.

2. Results and discussion

As the case study we have chosen β-arylthioalkylation of various π-donors with a number of β-arylthioalkyl chlorides, the reaction that had been thoroughly investigated previously in our group and was shown to proceed efficiently in the presence of various Lewis acid catalysts (Scheme 1).[11]



Scheme 1. β-Arylthioalkylation of π-donors; general scheme.

β-Arylthioalkyl chlorides **6**–**10**, which were employed as the electrophilic components in this study, were prepared in situ in quantitative yields via the standard Ad_E reaction of an arylsulfenyl chloride with the respective alkenes **1**–**5** (Table 1, for the details see Ref. 11).

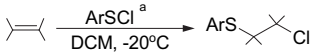
Alkene substrates were selected to represent different classes of electron rich carbon–carbon double bonds while the aryl moiety of sulfide (*p*-chlorophenyl) was chosen on the basis of its minimal steric demands and intermediate electron withdrawing strength.

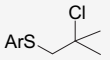
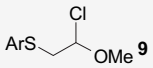
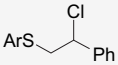
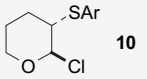
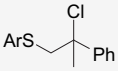
The choice of covalent π-donors was made to demonstrate different substitution pattern within a range of several orders of nucleophilicity magnitude according to Mayr's scale (Fig. 1).[12]

* Corresponding author. Tel.: +1 301 405 6136; fax: +1 301 314 9121.
E-mail address: moratn@umd.edu (M.O. Ratnikov).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.01.045

Table 1
Preparation of β-arylthioalkyl chlorides



Alkene	Adduct	Alkene	Adduct
 **1**	 **6**	 **4**	 **9**
 **2**	 **7**	 **5**	 **10**
 **3**	 **8**		

[a] Ar=p-ClC_6H_4.

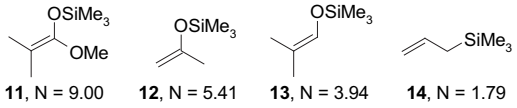
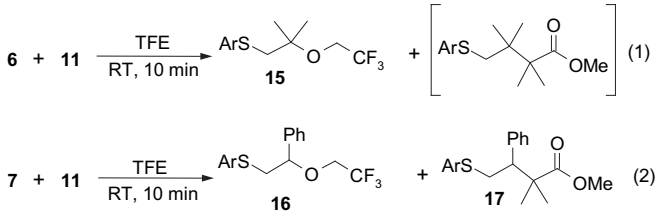


Figure 1. Carbon nucleophiles employed.

Initially, a reaction between the adduct **6** and the most reactive nucleophile **11** (in ratio 1:2) was studied in TFE solution at room temperature. The first results turned out to be rather discouraging due to an almost instantaneous formation of solvolysis product **15** according to TLC analysis (Scheme 2, Eq. 1). The latter adduct did not undergo any changes upon the storage of the reaction mixture overnight at this temperature even if an additional 5 equiv of **11** were added. The product **15** was shown to be unstable during chromatographic purification but its identity was fully confirmed by ^{1}H NMR data.



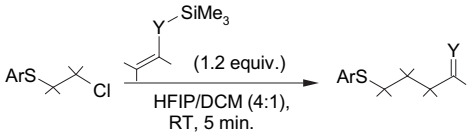
7/11	Conditions	16/17
1 : 2	TFE, RT, 5 min	90 : 10
1 : 10	TFE, RT, 5 min	59 : 32
1 : 10	TFE/CH_2Cl_2, RT, 5 min	35 : 62

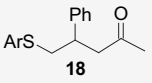
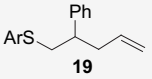
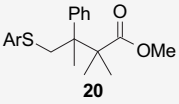
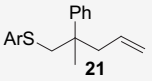
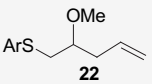
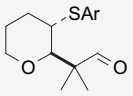
Scheme 2. β-Arylthioalkylation in TFE.

To facilitate the formation of the desired C–C coupling product, the electrophilic component was changed to the styrene adduct **7** that might form a substantially more stable benzylic cationic intermediate and thus should be more prone to react with carbon nucleophiles. Here again the formation of solvoadduct **16** was observed but at the same time the ^{1}H NMR analysis of the reaction mixture indicated the presence of some amount (ca. 10%) of the desired product **17** (Scheme 2, Eq. 2). The yield of the latter could be increased up to 32% if the reaction was performed with the use of the substantial excess of the nucleophile **11** (up to 10 equiv). Since it was observed that the mixture of **7** and **11** is only partially soluble in TFE the next run was carried out in the mixed TFE/CH_2Cl_2 (4:1) solvent to ensure homogeneity. Under these conditions the compound **17** was formed as a major product, albeit the formation of **16** was not totally suppressed. It was also observed that the order of the reagent mixing might critically affect the reaction outcome. The best yield was obtained if TFE was added the last to the solution of **7** and **11** in CH_2Cl_2. The reverse order, namely first dissolving **7** in TFE/CH_2Cl_2 (4:1) and then (after 5–7 min) adding of **11** to this solution resulted in a nearly complete formation of the solvoadduct **16**.

The above results attested to the viability of the suggested approach toward the electrophilic activation of the covalent β-arylthioalkyl chlorides and encouraged further development. The next logical step was a replacement of TFE with less nucleophilic HFIP.[13] This modification turned out to be essential in our efforts to tweak the reaction toward an exclusive formation of the alkylation products. In fact, it was discovered that in HFIP/CH_2Cl_2 medium interaction of β-arylthioalkyl chlorides **7**–**10** with the carbon nucleophiles **11**–**14** proceeds smoothly and gives the target products **18**–**23** in good to excellent yields (see Table 2).

Table 2
β-Arylthioalkylation in HFIP



Electrophile	Nucleophile	Product	Yield
7	**12**	 **18**	88%
7	**14**	 **19**	93%
8	**11**	 **20**	72%
8	**9**	 **21**	58%
9	**9**	 **22**	81%
10	**13**	 **23**	62%[a]

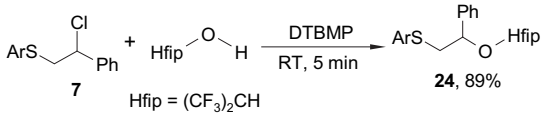
[a] In this case the reaction was carried out at 0 °C; otherwise an extensive decomposition was observed.

The general reaction procedure involves an in situ preparation of the electrophiles **7**–**10** in CH_2Cl_2 at −20 °C, followed by the addition of 1.2 equiv of nucleophilic components **11**–**14**, and introduction of HFIP at ambient temperature. According to the TLC data, the reaction is complete within 5 min. Subsequent removal of the solvent and volatile by-products as a rule is sufficient for the isolation of the products as individual compounds.

Remarkably, no detectable amounts of solvoadducts were formed under the above conditions. Moreover, no substantial solvolysis of the starting chloroadducts occurred upon their storage for several hours at room temperature in the absence of an external nucleophile.

At the same time, the solvolysis could be easily achieved upon the addition of equimolar amounts of 2,6-di-*tert*-butyl-4-

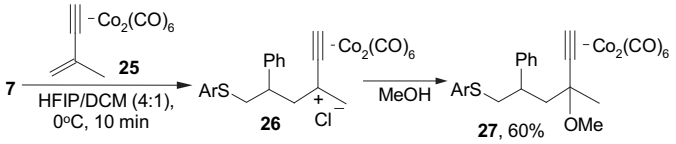
methylpyridine (DTBMP) to the above solution as exemplified by the conversion of **7** into the respective HFIP-derivative **24** (Scheme 3). The latter was shown to be totally unreactive toward π-nucleophiles even upon reflux in HFIP solution.



Scheme 3. Preparation of the solvoadduct.

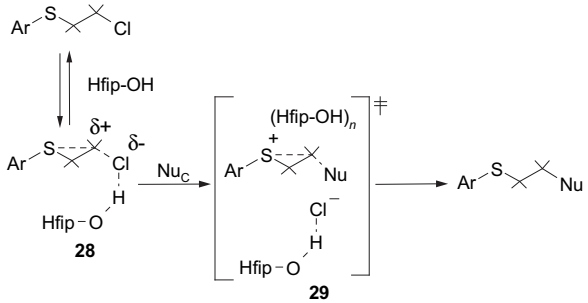
The set of the precursors shown in Table 2 includes the major structural types of the compounds that have most commonly been used in the similar transformations conventionally carried out in the presence of the stoichiometric amounts of various LA.[11] Consequently, we may conclude that the above results clearly indicate the generality of the suggested Lewis acid-free protocol as a convenient and mild procedure in order to perform β-arylthioalkylation of various π-donors.[14]

The applicability of developed procedure was also tested for the reaction involving dicobalthexacarbonyl (DCHC) complexes of the conjugated enynes as the carbon nucleophile in β-arylthioalkylation (see Scheme 4). The presented example demonstrates the opportunity to perform the acid-free β-arylthioalkylation of the alkenes like **25** that are substantially less nucleophilic than above-shown Si-capped derivatives.[12] In line with the previous evidence[11] we suggested that the interaction of **7** with **25** resulted in the initial formation of the cationoid intermediate **26** that should be sufficiently stable in the solution and could be trapped by external nucleophiles to give the products of 1,2-addition across the double bond of the starting substrate **25**. It was found that methanol is especially efficient as such a quencher as is shown by the formation of the adduct **27**.[15] However, the attempts to employ at this step carbon nucleophiles (Nu_C) such as 2-silyloxypropene **12** failed—no reaction occurred at 0 °C and a complete decomposition was observed during the storage at room temperature.



Scheme 4. β-Arylthioalkylation of DCHC complex.

We propose that the observed unusual activity pattern of HFIP is mostly due to its exceptionally high ionizing power[2,3] coupled with its low nucleophilicity[4] and extraordinary capacity to form strong hydrogen bonds with various hydrogen-bond acceptors.[5,6a] These unique properties might not only facilitate the transformation of the starting covalent chloride[16] into a polarized intermediate complex **28** (Scheme 5) thus enhancing the electrophilicity of the former but also provide an efficient driving force for the formation of the polar transition state **29** additionally stabilized by the efficient solvation of the chloride anion by the solvent molecules.[17,18] In other words the medium effect of HFIP could be explained in terms of the electrophilic solvent assistance in a way similar to the one employed for the interpretation of solvolytic data of tertiary butyl derivatives (see, for example, data in Ref. 19).



Scheme 5. A plausible mechanism.

3. Conclusion

In conclusion, we have developed a novel method of β-arylthioalkylation of silyl-containing π-donors with the readily available covalent electrophiles in the absence of Lewis acids. The essential role of HFIP as the sole promoter of the reaction was established. The elaborated procedure allows preparation of the respective products of C-alkylation in good to excellent yields while avoiding the utilization of costly and/or toxic heavy metal catalysts. This study served as a prologue for the further investigation which revealed the generality of the observed electrophilic activation effects for a number of other types of Friedel–Crafts alkylations.[10]

4. Experimental

4.1. General information

All experiments were carried out under dry argon using anhydrous solvents purified using the standard methods. TLC analysis was carried out on plates with silica. Column chromatography was performed using silica gel (220–240 mesh ASTM). Chemical shifts are reported in parts per million as follows: chemical shift (δ), multiplicity (s=singlet, d=doublet, m=multiplet, etc.), coupling constant (J, in Hertz), and integration.

p-Chlorobenzene sulfenyl chloride was prepared as described previously.[20] Silyl ketene acetal **11**[21] and silyl ethers **12**,**13**[22] were prepared using the described methods. Other reagents were used as received from commercial sources unless otherwise noted.

4.2. Preparation of methyl 2,2-dimethyl-3-phenyl-4-[4-chlorophenylthio]-butanoate (17) and α-[2,2,2-trifluoroethoxy]-β-[4-chlorophenylthio]-ethylbenzene (16)

Method A: biphasic reaction in TFE. A solution of styrene (104 mg, 1.0 mmol) in a dry dichloromethane (2.0 ml) was cooled to −20 °C and 4-chlorobenzenesulfenyl chloride (179 mg, 1.0 mmol) was added. The reaction was stirred for 5 min at −20 °C and was warmed to room temperature. The solvent was rapidly evaporated under reduced pressure. Silyl ketene acetal **11** (1.74 g, 10.0 mmol) followed by TFE (2.0 ml) were added to the colorless residue. After 15 min the reaction mixture was evaporated on a rotary evaporator. The residue was dissolved in a small volume of hexane. After purification with column chromatography (hexane/ethyl acetate, 10:1) a colorless oil of *C*-adduct **17** (112 mg, 32%) and a colorless oil of solvoadduct **16** (205 mg, 59%) were obtained.

Method B: monophasic reaction in TFE/DCM (4:1) mixture. A solution of 4-chlorobenzenesulfenyl chloride (90 mg, 0.50 mmol) in a dry dichloromethane (0.50 ml) was cooled to −20 °C and styrene (52 mg, 0.50 mmol) was added. The reaction was stirred for 5 min at −20 °C and was warmed to room temperature. Silyl ketene acetal **11** (870 mg, 5.0 mmol) followed by TFE (2.0 ml) was added to the resulting mixture. After 1 h the reaction mixture was evaporated on a rotary evaporator. The residue was dissolved in a small volume of hexane. After purification with column chromatography (hexane/ethyl acetate, 10:1) a colorless oil of *C*-adduct **17** (108 mg, 62%) and a colorless oil of solvoadduct **16** (63 mg, 35%) were obtained.

Compound **17**: R_f=0.34 in hexane/ethyl acetate (10:1).

^{1}H NMR ($CDCl_3$, 500 MHz): 1.06 and 1.17 (both s, 3H each), 3.22 (m, 2H), 3.30 (m, 1H), 3.63 (s, 3H), 7.12 (d, J=7.3, 2H), 7.17 and 7.22 (both d, J=8.2, 2H each), 7.29 (m, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 20.8, 25.0, 35.7, 46.6, 51.9, 52.3, 127.3, 128.0, 128.9, 129.6, 131.1, 132.1, 134.9, 138.4, 177.3.

Anal. Calcd for $C_{19}H_{21}ClO_2S$: C, 65.41; H, 6.07; found: C, 65.24; H, 6.39.

Compound **16**: R_f=0.38 in hexane/ethyl acetate (10:1).

^{1}H NMR ($CDCl_3$, 500 MHz): 3.15 (dd, J_1=13.7, J_2=7.4, 1H), 3.37 (dd, J_1=13.7, J_2=5.5, 1H), 3.65 and 3.72 (both m, 1H each), 4.54 (dd, J_1=7.4, J_2=5.5, 1H), 7.22–7.40 (m, 9H).

Anal. Calcd for $C_{16}H_{14}ClF_3OS$: C, 55.41; H, 4.07; found: C, 55.72; H, 4.25.

4.3. General procedure for the reactions presented in Table 2. β-Arylthioalkylation in HFIP

A solution of 4-chlorobenzenesulfenyl chloride (90 mg, 0.50 mmol) in dry DCM (0.50 ml) was cooled to −20 °C and alkene (0.50 mmol) was added. The mixture was stirred for 5 min at −20 °C and was warmed to 0 °C. Nucleophile (0.60 mmol) followed by HFIP (2.0 ml) were added to the resulting colorless solution. After 5 min the reaction mixture was evaporated on a rotary evaporator. The residue was dissolved in a small volume of hexane and the product was purified with flash chromatography (hexane/ethyl acetate). Fractions containing the product were combined and the solvent was evaporated.

*4.3.1. 4-Phenyl-5-[4-chlorophenylthio]-pentanone-2 (**18**).* Yield 88%; R_f=0.27 in hexane/ethyl acetate (10:1).

^{1}H NMR ($CDCl_3$, 500 MHz): 1.98 (s, 3H), 2.75 (dd, J_1=17.1, J_2=7.9, 1H), 2.96 (dd, J_1=17.1, J_2=6.7, 1H), 3.08 (m, 2H), 3.35 (m, 1H), 7.08–7.34 (m, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): 30.6, 40.2, 40.3, 48.7, 127.1, 127.5, 128.7, 129.1, 130.7, 132.1, 134.7, 142.6, 206.8.

Anal. Calcd for $C_{17}H_{17}ClOS$: C, 66.98; H, 5.62; found: C, 67.18; H, 5.70.

*4.3.2. 4-Phenyl-5-[4-chlorophenylthio]-pentene-1 (**19**).* Yield 93%; R_f=0.42 in hexane/ethyl acetate (40:1).

^{1}H NMR ($CDCl_3$, 300 MHz): 2.49 and 2.64 (both m, 1H each), 2.92 (m, 1H), 3.17 and 3.24 (both dd, J_1=13.4, J_2=7.3, 1H), 5.01 (d, J=8.8, 1H), 5.05 (d, J=15.4, 1H), 5.62 (m, 1H), 7.18–7.36 (m, 9H).

^{13}C NMR ($CDCl_3$, 75 MHz): 39.7, 40.1, 45.0, 116.9, 126.7, 127.6, 128.4, 128.9, 130.4, 131.7, 135.7, 142.9.

Anal. Calcd for $C_{17}H_{17}ClS$: C, 70.69; H, 5.93; found: C, 70.75; H, 5.93.

*4.3.3. 2,2,3-Trimethyl-3-phenyl-4-[4-chlorophenylthio]-butanoate (**20**).* Yield 72%; R_f=0.36 in hexane/ethyl acetate (10:1).

^{1}H NMR ($CDCl_3$, 500 MHz) 1.11 (s, 3H), 1.19 (s, 3H), 1.60 (s, 3H), 3.33 (d, J=12.2, 1H), 3.57 (s, 3H), 4.09 (d, J=12.2, 1H), 7.20–7.34 (m, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) 21.3, 21.8, 22.4, 42.7, 47.2, 50.0, 51.6, 126.7, 127.5, 128.2, 128.9, 130.6, 131.6, 136.9, 141.2, 176.6.

Anal. Calcd for $C_{20}H_{23}ClO_2S$: C, 66.19; H, 6.39; found: C, 66.52; H, 6.54.

*4.3.4. 4-Methyl-4-phenyl-5-[4-chlorophenylthio]-pentene-1 (**21**).* Yield 58%; R_f=0.37 in hexane/ethyl acetate (40:1).

^{1}H NMR ($CDCl_3$, 500 MHz): 1.48 (s, 3H), 2.52 (dd, J_1=13.4, J_2=7.9, 1H), 2.64 (dd, J_1=14.0, J_2=6.7, 1H), 3.21 (d, J=12.2, 1H), 3.35 (d, J=12.2, 1H), 5.02 (d, J=9.8, 1H), 5.07 (d, J=17.0, 1H), 5.56 (m, 1H), 7.19 (m, 4H), 7.24 (m, 1H), 7.34 (m, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz): 24.3, 42.0, 46.1, 47.9, 118.1, 126.3, 126.4, 128.2, 128.8, 130.7, 131.8, 134.2, 136.4, 145.3.

Anal. Calcd for $C_{18}H_{19}ClS$: C, 71.38; H, 6.32; found: C, 71.05; H, 6.14.

*4.3.5. 4-Methoxy-5-[4-chlorophenylthio]-pentene-1 (**22**).* Yield 81%; R_f=0.42 in hexane/ethyl acetate (10:1).

^{1}H NMR ($CDCl_3$, 500 MHz): 1.09 (s, 3H), 1.11 (s, 3H), 1.60 (m, 3H), 2.15 (m, 1H), 2.88 (m, 1H), 3.35 (m, 1H), 3.46 (d, J=10.4, 1H), 3.96 (m, 1H), 7.25 (m, 4H) 9.63 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz): 16.7, 20.5, 26.7, 32.8, 47.4, 50.2, 68.4, 83.3, 129.1, 131.9, 133.5, 133.7, 202.1.

Anal. Calcd for $C_{15}H_{19}ClO_2S$: C, 60.29; H, 6.41; found: C, 60.58; H, 6.56.

4.3.6. 2-[(2R,3R*)-3-(4-chlorophenylthio)-tetrahydro-2H-pyran-2-yl]-2-methyl-propanal (**23**).* Yield 62%; R_f=0.64 in hexane/ethyl acetate (40:1).

^{1}H NMR ($CDCl_3$, 500 MHz): 2.41 (t, J=5.9, 2H), 2.99 (dd, J=13.1 and 5.9, 1H), 3.06 (dd, J=13.1 and 5.9, 1H), 3.37 (s, 3H), 3.33–3.48 (m, 1H), 5.10 (d, J=11.1, 1H), 5.11 (d, J=15.8, 1H), 5.69–5.92 (m, 1H), 7.24 (d, J=8.5, 2H), 7.30 (d, J=8.5, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): 37.2, 37.6, 57.1, 79.3, 177.8, 128.9, 130.7, 131.9, 133.7, 135.3.

Anal. Calcd for $C_{12}H_{15}ClOS$: C, 59.37; H, 6.23; found: C, 60.76; H, 6.76.

4.4. Preparation of α-[1,1,1,3,3,3-hexafluoroisopropoxy]-β-[4-chlorophenylthio]-ethylbenzene (24)

A solution of 4-chlorobenzenesulfenyl chloride (90 mg, 0.50 mmol) in dry DCM (0.50 ml) was cooled to −20 °C and styrene (52 mg, 0.50 mmol) was added. The reaction mixture was stirred for 5 min at −20 °C and was warmed to room temperature. A solution of 2,6-di-*tert*-butyl-4-methylpyridine (123 mg, 0.60 mmol) in HFIP (2.0 ml) was added. After 5 min the reaction mixture was evaporated on a rotary evaporator. The residue was dissolved in a small volume of hexane and the product was purified with flash chromatography (hexane/ethyl acetate, 10:1, R_f=0.39). Fractions containing the product were combined and the solvent was evaporated under reduced pressure. A colorless oil of solvoadduct (185 mg, 89%) was obtained.

^{1}H NMR ($CDCl_3$, 500 MHz): 3.22 and 3.51 (both dd, J_1=13.7, J_2=6.7, 1H each), 4.00 (sept, J=6.1, 1H), 4.81 (t, J=6.7, 1H) 7.25 (m, 4H), 7.32 (m, 2H), 7.41 (m, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 30.1, 40.8, 72.8 (sept, J=32.6), 120.8 (q, J=286.0), 122.0 (q, J=286.0), 127.9, 129.0, 129.1, 129.8, 131.3, 132.6, 134.0, 136.2.

^{19}F NMR ($CDCl_3$, 470 MHz): −68.1, −66.9.

Anal. Calcd for $C_{17}H_{13}ClF_6OS$: C, 49.23; H, 3.16; found: C, 49.44; H, 3.35.

4.5. Preparation of DCHC complex of 3-methyl-3-methoxy-5-phenyl-6-[(4-chlorophenylthio)]-hex-1-yne (27)

A solution of 4-chlorobenzene sulfenyl chloride (90 mg, 0.50 mmol) in dry DCM (0.50 ml) was cooled to −20 °C and styrene (52 mg, 0.50 mmol) was added. The reaction mixture was stirred for 5 min at −20 °C and was warmed to 0 °C. A solution of DCHC complex of isopropenylacetylene **25** (176 mg, 0.50 mmol) in DCM (0.50 ml) followed by HFIP (4.0 ml) were added. After 15 min the reaction mixture was poured into MeOH (10 ml) at −30 °C. The resulting solution was treated with saturated aqueous $NaHCO_3$ (10 ml) and extracted with hexane. The organic phase was filtered through a plug of silica gel (eluent/hexane/ethyl acetate, 10:1). The filtrate was evaporated under reduced pressure (bath temperature was kept below 30 °C to avoid DCHC complex decomposition). The residue was purified with flash chromatography (hexane/ethyl

acetate, 10:1) to give product **27** as a 3:1 diastereomeric mixture (inseparable, 379 mg, 60%).

^{1}H NMR ($CDCl_3$, 500 MHz): 1.43 (s), 3H; 2.18 (dd, J_1=14.7, J_2=3.7), 1H; 2.32 (dd, J_1=14.7, J_2=7.3) and 2.49 (dd, J_1=14.7, J_2=3.6), 1H in total; 2.32 (d, J=7.0), 1H; 2.49 (d, J=7.0), 1H; 3.23–3.40 (m), 1H; 6.00 (s) and 6.10 (s), 1H in total; 7.15–7.33 (m), 9H.

^{13}C NMR ($CDCl_3$, 125 MHz): 26.8 and 27.7, 40.9 and 41.3, 41.8 and 42.6, 46.1 and 47.2, 50.0 and 50.1, 64.7, 73.4, 78.8 and 79.2, 126.6 and 126.7, 127.7 and 127.8, 128.4 and 128.7, 128.9 and 129.0, 130.6 and 130.8, 132.0, 134.9, 144.6.

Acknowledgements

Financial support of RFBR (project no 09-03-00666) and the Presidium RAS Program (18P-2009) is gratefully acknowledged.

References and notes

1. For a review, see: (a) Bégué, J.-P.; Bonnet-Delpon, D.; Crousse, B. *Synlett* **2004**, 18; (b) Shuklov, I. A.; Dubrovina, N. V.; Börner, A. *Synthesis* **2007**, 2925.
2. According to the results of solvatochromic studies an empirical parameter of solvent polarity, E_N^T=1.068 for HFIP and 0.898 for TFE. Among 360 solvents tested, HFIP is the sole solvent outside the scale defined by the limiting values E_N^T=0 (for Me_4Si) and E_N^T=1 (for water), see: Reinhardt, C. *Chem. Rev.* **1994**, *94*, 2319.
3. From the solvolysis data it was estimated that solvent ionizing power $Y_{2\text{-AdOTs}}$=3.61 for HFIP and 1.80 for TFE (*cf.* with the values −0.61 for CH_3COOH and 3.04 for HCOOH); for reference see: Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
4. (a) Hoffmann, M.; Hampel, N.; Kanzian, T.; Mayr, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 5402; (b) Minegishi, S. S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, *126*, 5174.
5. (a) The enhanced ability of TFE and HFIP to donate a proton in a solvent-to-solute hydrogen bond could be illustrated by the comparison of the values of α-parameter for these solvents within the general scale containing the data for more than 300 solvents which was derived from the Kamlet–Taft generalized solvatochromic equation Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877; In fact, it was disclosed that α-parameters have the maximal values for TFE and HFIP (α=1.51 and 1.96 for TFE and HFIP correspondingly; cf. α=0.83 for ethanol, 1.12 for acetic acid and 1.17 for water; (b) HFIP was shown to form much stronger hydrogen bonds than phenol or ethanol with a number of neutral acceptors regardless of the experimental parameters employed for the evaluation of this property (−ΔH values from calorimetric data, shift in O–H -stretching frequencies or hydrogen-bond induced proton chemical shifts), see: Purcell, K. F.; Stikeleather, J. A.; Brunk, S. D. *J. Am. Chem. Soc.* **1968**, *91*, 4019; (c) The data of the conductivity studies for a number of tetraalkylammonium salts in TFE and especially HFIP shows a pattern consistent with a good solvation of anions due to the formation of strong hydrogen bonds and a rather poor cation solvation, see: Evans, D. F.; Nadas, J. A.; Matesich, M. A. *J. Phys. Chem.* **1971**, *75*, 1708; Matesich, M. A.; Knoefel, J.; Feldman, H.; Evans, D. F. *J. Phys. Chem.* **1973**, *77*, 366; (d) Determination of the gas phase anion-binding energy of some solvents with halide ions revealed that both TFE and especially HFIP are the strongest hydrogen bond donors, e.g., the bond strength for the chloride ion >10 kcal greater in comparison to water or methanol, see: Caldwell, G. W.; Masucci, J. A.; Ikonomou, M. G. *Org. Mass Spectrom.* **1989**, *24*, 8; (e) For a general discussion of the TFE and HFIP properties, see also: Eberson, L.; Hartshorn, M. P.; Persson, O.; Radner, F. *Chem. Commun.* **1996**, 2105.
6. (a) Allard, B.; Casadevall, A.; Casadevall, E.; Largeau, C. *Nouv. J. Chim.* **1979**, *3*, 335; (b) Allard, B.; Casadevall, A.; Casadevall, E.; Largeau, C. *Nouv. J. Chim.* **1980**, *4*, 539; (c) Leonard, N. J.; Neelima. *Tetrahedron Lett.* **1995**, *36*, 7833; (d) Magueur, G.; Crousse, B.; Ourévitch, M.; Bégué, J.-P.; Bonnet-Delpon, D. *J. Org. Chem.* **2003**, *68*, 9763.
7. Das, U.; Crousse, B.; Kesavan, V.; Bonnet-Delpon, D.; Bégué, J.-P. *J. Org. Chem.* **2000**, *65*, 6749.
8. (a) Trahanovsky, W. S.; Doyle, M. P. *Tetrahedron Lett.* **1968**, *18*, 2155; (b) Lambert, J. B.; Featherman, S. I. *J. Am. Chem. Soc.* **1977**, *99*, 1542.
9. (a) Ferber, P. H.; Gream, G. E. *Aust. J. Chem.* **1981**, *34*, 1051; (b) Ferber, P. H.; Gream, G. E. *Aust. J. Chem.* **1981**, *34*, 2217.
10. Ratnikov, M. O.; Tumanov, V. V.; Smit, W. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9739.
11. Smit, W. A.; Smolyakova, I. P.; Caple, R. *Chem. Rev.* **1994**, *94*, 2359; See also: Smit, W. A.; Lazareva, M. I.; Smolyakova, I. P.; Caple, R. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 1949.
12. Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500.
13. *N* (TFE)=1.2; *N* (HFIP)=−2.4 according to Ref. 4b.
14. A limitation of the reaction scope is also to be commented. In fact, the trial experiments with the electrophile **6** revealed that its interaction with π-donors **11** and **12** in HFIP proceeds non-selectively to give mixture of products.
15. The compound **27** was obtained previously with the use of equimolar amounts of $TiCl_4$ as the catalyst; for the details see: Lazareva, M. I.; Nguyen, S. T.; Nguyen, M. C.; Emiru, H.; McGrath, N. A.; Caple, R.; Smit, W. A. *Mendeleev Commun.* **2001**, 224.
16. Notably, one should consider these chlorides as real electrophiles involved since no reaction with nucleophiles was observed for the respective solvoadducts like **24** (and also **16**); vide supra.
17. The use of HFIP as an optimal solvent for the generation of persistent carbocations and cationic radicals is well-documented in the literature; see Ref. 5d for the pertinent examples, see also: Eberson, L.; Hartshorn, M. P.; Persson, O. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1735; Eberson, L.; Hartshorn, M. P.; Persson, O. *J. Chem. Soc., Perkin Trans. 2* **1996**, 141; McClelland, R. A.; Mathivanan, N.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 4857; Cozens, F. L.; McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1993**, *115*, 5050; McClelland, R. A.; Chan, C.; Cozens, F.; Modro, A.; Steenken, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1337.
18. It should be emphasized that while the involvement of episulfonium ions as the discrete intermediates had been firmly established for a number of examples of the Lewis acid promoted β-arylthioalkylation reactions (see data in Ref. 11) we do not see any compelling reasons to consider this mechanism as an alternative to the one shown in Scheme 5.
19. Fărcasiu, D.; Jähme, J.; Rüchardt, C. *J. Am. Chem. Soc.* **1985**, *107*, 5717.
20. Harpp, D. N.; Friedlander, B. T.; Smith, R. A. *Synthesis* **1979**, *3*, 181.
21. Ainsworth, C.; Chen, F.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 59.
22. Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2075.