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TRIFLUOROACETYLTRIPHENYLSILANE AS A POTENTIALLY USEFUL FLUORINE-CONTAINING BUILDING BLOCK. PREPARATION AND ITS TRANSFORMATION INTO 2,2-DIFLUORO ENOL SILYL ETHERS

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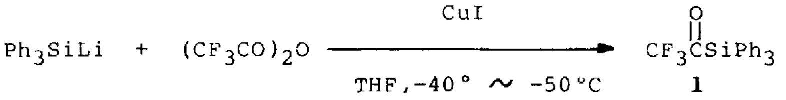
Abstract: The first example of perfluoroacylsilanes—trifluoroacetyltriphenylsilane was prepared in good yield and it has been converted into a series of 2,2-difluoro enol silyl ethers in almost quantitative yields by treatment with various organolithiums.

Methods for the synthesis of fluorinated organics with fluorine atom(s) substituted at a specific site have received a growing interest in recent years, because many of these compounds exhibit interesting biological activity and high performance in material science[1]. Therefore, development and transformation of fluorine-containing building blocks are the important synthetic needs in this area[2]. As we know, acylsilanes are now becoming an important class of synthetic intermediates[3] since Brook's first observation in 1957[4] that a carbonyl group located α to a silicon atom display unusual reactivity. Despite the wealth of information accumulated on acylsilanes, no description on the preparation of perfluoroacylsilanes and their utilization in organic synthesis has been known. In conjunction with our program aimed at search for new versatile and useful fluorine-containing building blocks, we became interested in exploring the synthesis of trifluoroacetyltriphenylsilane(**1**) and its utilization as a potentially useful fluorine-containing building block. Herein, we wish to report a convenient synthesis of **1** and its facile transformation into 2,2-difluoro enol silyl ethers(**2**).

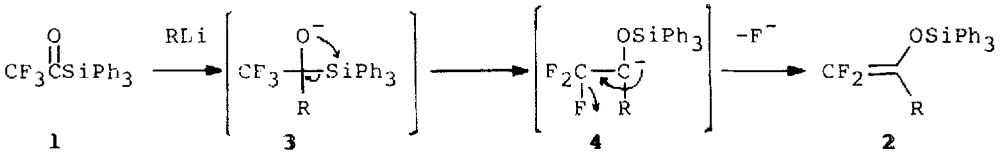
In 1978 Duffaut et al[5] reported the synthesis of alkanoylsilanes through the coupling of a silyl copper, which was formed in situ by the reaction of silyl lithium reagent with a stoichiometric amount of cuprous iodide, with alkanoyl chlorides in modest yields. Initially, we attempted to prepare the trifluoroacetyltriphenylsilane by this method from triphenylsilyl copper and trifluoroacetyl chloride, but the desired product was obtained only in rather poor yield, around 30%. After several trials, we found that simply on replacing trifluoroacetyl chloride by the corresponding acid anhydride the yield of trifluoroacetyltriphenylsilane could be significantly improved, up to 75% (eq.1)[6].



$$Ph_3SiLi + (CF_3CO)_2O \xrightarrow[\text{THF},-40^\circ \sim -50^\circ C]{CuI} \underset{\mathbf{1}}{CF_3\overset{O}{\overset{\|}{C}}SiPh_3} \qquad (eq.1)$$

Compound **1** is a pale yellow crystalline solid, melts at 122°C and has a carbonyl stretching absorption frequency at 1685 cm^{-1}; ^1H NMR(CCl_4) δ 7.20-7.90(m) ^{19}F NMR(CCl_4) δTFA 1.6(s, upfield positive).

With trifluoroacetyltriphenylsilane(**1**) in hand, we then undertook the study of its reactivity. We found that when 1 was treated with an organolithium reagent either in THF or Et_2O, a product, which was identified to be a 2.2-difluoro enol silyl ether(**2**), was produced in an almost quantitative yield. This reaction could also take place even in hexane, although with a somewhat lower yield. The formation of 2.2-difluoro enol silyl ethers may result through a sequence of nucleophilic addition of RLi, C to O silyl rearrangement[7](Brook rearrangement, **3**→**4**) and β-elimination of fluorine, as shown in eq.2.

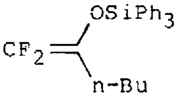
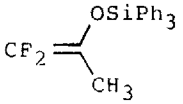
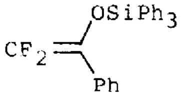
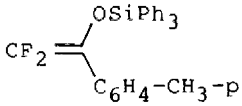
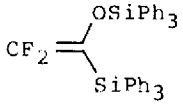


(eq.2)

The general procedure is as follows: To a solution of trifluoroacetyltriphenylsilane(**1**,0.5mmol) in THF(4ml) cooled at -78°C was added via syringe an equivalent amount of organolithium reagent and stirring was continued at -78°C for 15 min. After warming up to room temperature, water (10ml) was added and the mixture was extracted with ether (3X10ml). The ethereal solution was washed with brine, dried over anhydrous sodium sulfate and concentrated. The resulting residue was chromatographed on silica gel using a 99:1 mixture of petroleum ether(60-90°C) and ethyl acetate as the eluent to afford the 1,1-difluoro-2-triphenylsiloxy-1-alkenes(**2**).

The results are summarized in Table 1. To our knowledge, the only existing method of generating 2,2-difluoro enol silyl ethers is that reported by Ishihara et al[9], who obtained the 1,1-difluoro-2-trimethylsiloxy-1-alkenes in moderate yields by the treatment of chlorodifluoromethyl ketones with

Table 1. Preparation of 2,2-difluoro enol silyl ethers(**2**)

RLi	Solvent	Enol silyl ethers[8]		Yield(%)
n-BuLi	THF	 $CF_2{=}C(OSiPh_3)(n\text{-}Bu)$	(**2a**)	95
n-BuLi	Et_2O	**2a**		96
n-BuLi	Hexane	**2a**		88
CH_3Li	THF	 $CF_2{=}C(OSiPh_3)(CH_3)$	(**2b**)	99
PhLi	THF	 $CF_2{=}C(OSiPh_3)(Ph)$	(**2c**)	90
p-$CH_3C_6H_4Li$	THF	 $CF_2{=}C(OSiPh_3)(C_6H_4\text{-}CH_3\text{-}p)$	(**2d**)	89
Ph_3SiLi	THF	 $CF_2{=}C(OSiPh_3)(SiPh_3)$	(**2e**)	91

zinc dust in the presence of chlorotrimethylsilane at elevated temperatures. Thus the present reaction provides a novel and efficient synthesis of 2,2-difluoro enol silyl ethers under very mild condition and with excellent yields.

Like the 1,1-difluoro-2-trimethylsiloxy-1-alkene reported by Ishihara[9], the 1 1-difluoro-2-triphenylsiloxy-1-alkene(**2**) obtained in the present study was also able to undergo condensation with a variety of aldehydes and ketones in the presence of $TiCl_4$ to afford the corresponding α,α-difluoro-β-hydroxy-ketones in very good yields[10]. Further investigation on the utilization of trifluoroacetyltriphenylsilane as fluorine-containing building block for synthesizing fluorinated organics is in progress.

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References and Notes

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2. See, for examples: (a) T. Fuchikami, J. Synth. Org. Chem. Jpn., **42**, 775 (1984). (b) K. Tanaka, J. Synth. Org. Chem. Jpn., **48**, 16 (1990).
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6. It is noteworthy that this procedure is also applicable to the synthesis of pentafluoropropionyltriphenylsilane(83% yield, m.p. 85-87°C, ν(C=O), 1690cm^{-1}) and heptafluoro-n-butyryltriphenylsilane(74% yield, m.p. 42-44°C, ν(C=O),1690cm^{-1}) by starting from the corresponding acid anhydride and thus provides a general method of synthesizing perfluoroacylsilanes.
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8. **2a**, oil; ^{1}H NMR(CCl$_4$) δ 0.74(t,J=5Hz,3H),1.05-1.55(m,4H),1.75-2.05(m,2H), 7.05-7.95(m,15H); ^{19}F NMR(CCl$_4$) δ_{TFA} 26.4(d,J=90Hz,1F),42.0(d,J=90Hz,1F); IR(neat) 1770,1590,1250,1120,740,710 cm^{-1}; MS,m/e,394(M$^+$). **2b**, m.p.52.5-53.5°C; ^{1}H NMR(CCl$_4$) δ 1.6(t,J=4Hz,3H),7.10-7.80(m,15H); ^{19}F NMR(CCl$_4$) δ_{TFA} 28.5(dq,J=90Hz and 4Hz,1F),45.5(dq,J=90Hz and 4Hz, 1F);IR(KBr) 1780,1590, 1480,1250,1120,740,700 cm^{-1};MS,m/e,352(M$^+$). **2c**,m.p.59-61°C; ^{1}H NMR(CCl$_4$) δ 7.00-7.60(m); ^{19}F NMR(CCl$_4$), δ_{TFA} 20.8(d,J=70Hz,1F),36.0(d,J=70Hz,1F); IR (KBr) 1720,1580,1480,1260,1110,750,700 cm^{-1};MS,m/e,414(M$^+$). **2d**,oil; ^{1}H NMR (CCl$_4$) δ 2.24(s,3H),7.00-7.80(m,19H); ^{19}F NMR(CCl$_4$) δ_{TFA} 23.0(d,J=70Hz,1F), 38.0(d,J=70Hz,1F);IR(neat) 1720,1610,1590,1510,1480,1260,1120,840,740,700 cm^{-1}; MS,m/e,428(M$^+$). **2e**,m.p.143-144°c; ^{1}H NMR(CCl$_4$) δ 7.05- 7.75(m); ^{19}F NMR (CCl$_4$) δ_{TFA} 1.0(d,J=60Hz,1F), 27.1(d,J=60Hz,1F); IR(KBr) 1680,1580,1480, 1260,1100,740,690 cm^{-1};MS,m/e,596(M$^+$).
9. M. Yamana, T. Ishihara, T. Ando, Tetrahedron lett.,**24**,507 (1983).
10. R^{1}R^2-CH(OH)CF$_2$C(O)R. R=CH$_3$: R^1=p-O$_2$NC$_6$H$_4$, R^2=H (99%); R^1=o-BrC$_6$H$_4$, R^2=H (94%); R^1=Ph, R^2=H (93%); R^1=CH$_3$(CH$_2$)$_8$,R^2=H (83%);R^1=R^2=-(CH$_2$)$_5$- (74%); R=n-Bu: R^1=p-O$_2$NC$_6$H$_4$, R^2=H (97%).

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