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Preliminary Note

A convenient synthesis of 1-trifluoromethyl enol silyl ethers

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Abstract

Trifluoroacetyltriphenylsilane, on reaction with alkylidenetriphenylphosphoranes, gave rise exclusively to 1-trifluoromethyl enol silyl ethers. This reaction provides a new preparation of these fluorine-containing enol silyl ethers.

In contrast to the central position of enol silyl ethers in synthetic organic chemistry [1], fluorine-containing enol silyl ethers appear to have been much less exploited in organofluorine chemistry, mainly due to the difficulty of their synthesis. To date, only a few reports exist in the literature concerning the generation of these compounds [2]. However, in view of their potential utility as synthetic precursors for the construction of fluorine-containing molecules of biological interest [3], it is of much value to develop new and convenient methods for the generation of these enol silyl ethers.

Recently, we have reported a novel precursor of 2,2-difluoro enol silyl ethers, i.e. trifluoroacetyltriphenylsilane (**1**) [4]. As a part of our continuing studies on expanding the scope of utilization of **1**, we have found that **1** may also serve as a precursor for 1-trifluoromethyl enol silyl ethers. Thus, when **1** was treated with an alkylidenetriphenylphosphorane in Et_2O, 1-trifluoromethyl enol silyl ether (**2**) was obtained in good yield. Unstabilized or semi-stabilized phosphoranes could be used successfully in the present reaction, although a stabilized phosphorane failed to react with **1**. The results obtained are depicted in Table 1. The assignment of a *Z* or *E* configuration to the isomers in the products **2c**–**2e** was based on the general rule that the ^{19}F NMR signal of a CF_3 group attached to double bond will be shifted downfield when it is *cis* to the bulkier one of the two vicinal double-bond substituents relative to the position when they are in a *trans* orientation

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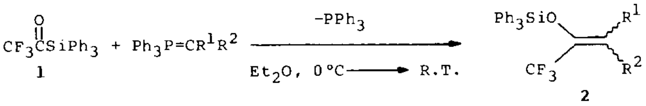
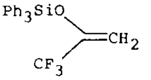
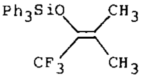
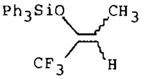
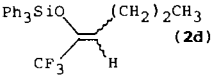
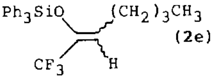
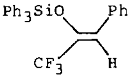
TABLE 1

Preparation of 1-trifluoromethyl enol silyl ethers[a]



$Ph_3P{=}CR^1R^2$		Enol silyl ethers (2)[b]	Yield (%)	$Z{:}E$[c]	^{19}F NMR δ_{TFA}[d]	
R^1	R^2				Z	E
H	H	 (2a)	81	–	−6.2[f]	
CH_3	CH_3	 (2b)	75	–	−3.2[f]	
H	CH_3	 (2c)	78	72:28	−5.0	−10.7
H	$(CH_2)_2CH_3$	 (2d)	70	86:14	−6.2	−11.1
H	$(CH_2)_3CH_3$	 (2e)	71	88:12	−6.1	−10.9
H	Ph	 (2f)	68	100:0	−7.1	–
H	CN	no reaction[e]				

[a] Et_2O was used as the solvent unless otherwise stated.

[b] All products have been fully characterized spectroscopically (IR, ^{19}F NMR, ^1H NMR spectroscopy and MS) and their elemental compositions determined by combustion analyses.

[c] The Z/E ratio was estimated by ^{19}F NMR spectroscopy.

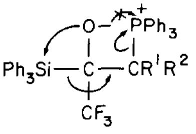
[d] ^{19}F NMR chemical shifts are shown in ppm downfield from external trifluoroacetic acid.

[e] THF was used as the solvent and the reaction mixture was refluxed for 12 h.

[f] No Z, E isomerism.

[5]. The assignment of the Z configuration to the product **2f** was made by correlation of its ^{19}F NMR shift with those of the products **2c**–**2e**.

Brook and Fieldhouse [6] have reported that, on reaction with phosphoranes, alkyl silyl ketones always result in the formation of a silylated alkene, e.g. the normal Wittig reaction product, whereas aryl silyl ketones lead to the formation of an enol silyl ether because of the ability of the aryl group to stabilize the negative charge generated on the adjacent carbon as a result of migration of the silicon moiety to oxygen. In the present case, it appears that the exclusive formation of an enol silyl ether can be attributed to the strong electron-withdrawing ability of the CF_3 group, which is capable of promoting charge transfer from silicon towards the carbon of the carbonyl group, as shown in Structure **3**. This attack of oxygen on silicon overrides that on phosphorus, thereby resulting in the elimination of triphenylphosphine.



3

To the best of our knowledge, the only existing method of generating 1-trifluoromethyl enol silyl ethers is that reported by Begue and Mesureur [2b], who obtained 1-trifluoromethyl enol silyl ethers in only low yield through the Wittig reaction of trimethylsilyl trifluoroacetate with an alkylidenephosphorane at elevated temperature. Thus, the present reaction provides a convenient synthesis of 1-trifluoromethyl enol silyl ethers under very mild conditions and in good yield.

In a typical experiment, $Ph_3P^+CH_3I^-$ (240 mg, 0.6 mmol) in dry Et_2O (2 ml) was added via a syringe to an ice-cooled suspension of an equivalent amount of Bu^nLi and stirring was continued for 30 min. A solution of trifluoroacetyltriphenylsilane (200 mg, 0.56 mmol) in dry Et_2O (2 ml) was then added and the mixture stirred at 0 °C for 1 h and then at room temperature for 3 h. Hexane (10 ml) was added and the solid portion was filtered off. The filtrate was concentrated under reduced pressure and the residue obtained was chromatographed on silica gel using petroleum ether (60–90 °C) as the eluent to give 3,3,3-trifluoro-2-triphenylsiloxypropene (**2a**) in 81% yield as a white solid, m.p. 82–84 °C. IR (KBr): 3030; 1650; 1590; 1360; 1180; 1120; 1000; 740; 720; 700 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 4.40 (d, $J=3.2$ Hz, 1H); 4.83 (d, $J=3.2$ Hz, 1H); 7.20–7.80 (m, 15H) ppm. ^{19}F NMR (CCl_4) δ_{TFA}: -3.2 (s) ppm. MS m/z (relative intensity): 370 (0.98); 369 (2.51); 259 (100). Analysis $C_{21}H_{17}F_3OSi$ requires: C, 68.08; H, 4.63; F, 15.39%. Found: C, 68.25; H, 4.48; F, 15.44%.

Acknowledgements

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References

1 E. W. Colvin, *Silicon in Organic Synthesis*, Butterworths, London, 1981.

2 See, for example: (a) M. Yamana, T. Ishihara and T. Ando, *Tetrahedron Lett.*, *24* (1983) 507; (b) J. P. Begue and D. Mesureur, *J. Fluorine Chem.*, *39* (1988) 271; (c) Y. Kobayashi, *Tetrahedron Lett.*, *29* (1988) 1803.

3 (a) M. Schlosser, *Tetrahedron*, *34* (1978) 3; (b) R. Filler and Y. Kobayashi, *Biomedicinal Aspects of Fluorine Chemistry*, Kodansha and Elsevier Biomedical, Tokyo, 1983.

4 F. Jin, B. Jiang and Y. Xu, *Tetrahedron Lett.*, *33* (1992) 1221.

5 (a) F. Camps, R. Canela, J. Coll, A. Messequer and A. Roca, *Tetrahedron*, *34* (1978) 2179; (b) F. Camps, F. J. Sanchez and A. Messequer, *Synthesis*, (1988) 823; (c) I. Kumadaki, M. Tamura, A. Ando, T. Nagai and M. Koyama, *Chem. Pharm. Bull.*, *36* (1988) 515; (d) D. Mead, K. Loh, A. E. Asato and R. S. H. Liu, *Tetrahedron Lett.*, *26* (1985) 2873; (e) J. P. Begue and D. Mesureur, *Synthesis*, (1989) 309; (f) T. Fuchikami, Y. Shibata and Y. Suzuki, *Tetrahedron Lett.*, *27* (1986) 3173.

6 A. G. Brook and S. A. Fieldhouse, *J. Organomet. Chem.*, *10* (1967) 235.