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Preliminary communication

Conversion of trifluoromethyl carbonyl compounds to the corresponding vinylsilanes with cyclopentadienyl *tris*(trimethylsilylmethyl)titanium(IV)

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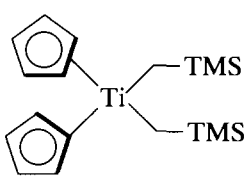
Abstract

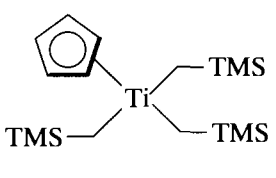
The conversion of trifluoromethyl ketones, esters, amides, and thioesters to their corresponding vinylsilanes using cyclopentadienyl *tris*(trimethylsilylmethyl)titanium(IV) has been investigated.

Keywords: Cyclopentadienyl *tris*(trimethylsilylmethyl)titanium(IV); (Trifluoromethyl)-vinylsilanes; Titanium; Vinylsilanes; Alkene; Perfluoroalkene

Percuring our interest in versatile synthons for the introduction of the trifluoromethyl group [1–3], we have investigated the synthesis of trifluoromethylvinylsilanes. They are potentially versatile because vinylsilanes react with a variety of electrophiles [4,5] and they serve as masked carbonyl compounds [6,7]. Recently a new method for the conversion of carbonyl compounds into vinylsilanes, by heating them with dicyclopentadienyl *bis*(trimethylsilylmethyl)titanium(IV) **1** or cyclopentadienyl *tris*(trimethylsilylmethyl)titanium(IV) **2** has been reported [8]. Among titanium-mediated olefinations with reagents such as the Tebbe's reagent [9] and those more recently reported by Petasis et al. [8,10–12] only one low-yielding example, with Tebbe's reagent and a trifluoromethylcarbonyl compound has been described [13]. We hoped that trifluoromethylvinylsilanes could be synthesised by olefination of trifluoromethyl carbonyl compounds with complex **2**, which has been shown to be the more reactive complex of the two titanium complexes towards carbonyl compounds [8].



(1)



(2)

In this commmunication we report our results on the reactions of complex **2** with a series of trifluoromethyl ketones, esters, amides and thioesters (Table 1). These olefinations were performed with 1.3 equivalent of complex **2** in toluene at 110°C in a sealed tube [14].

Ketones and esters were smoothly converted to the corresponding vinylsilanes with little Z/E stereoselectivity in good yield. Increasing the size of the ester group only decreased the rate of reaction and conversion with no significant effect on stereoselectivity. Amides are less reactive, with stereoselectivity depending upon the amino group. For thioesters the vinylsilanes were isolated only in low yield, although the starting ester was completely consumed. When stereoselectivity was observed, the E isomer predominated which is the opposite of the Wittig olefination of trifluoromethyl esters [1] and thioesters [2].

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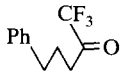
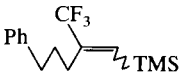
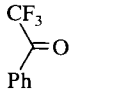
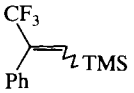
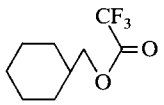
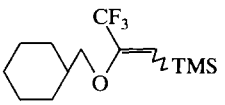
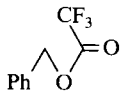
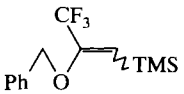
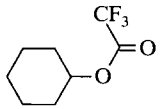
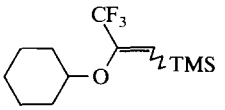
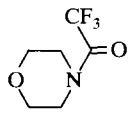
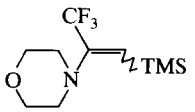
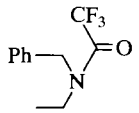
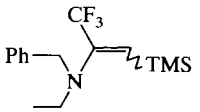
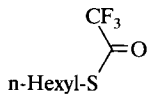
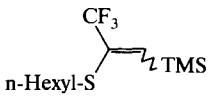
Table 1
Reaction of complex **2** with trifluoromethyl carbonyl compounds

Carbonyl compound	Product	Reaction Time H	Conversion %	Yield [a] %	$E:Z$ [b]
		18	100	80	1:1
		18	100	75	1:1
		24	100	65	1.75:1
		24	100	70	1.9:1
		48	80	50	2.1:1
		48	75	40	1:1
		48	70	42	3.5:1
		24	100	10	1:1

[a] Isolated yield [15], [b] isomer ratio calculated from ^{19}F NMR data [16].

References and notes

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[14] Typical procedure: A solution of 1,1,1,-trifluoro-5-phenylpentan-2-one [1] (0.5 g, 2.3 mmol) and cyclopentadienyl*tris*(trimethylsilylmethyl)titanium(IV) **2** [8] (1.12 g, 3 mmol) in toluene (20 ml) was heated at 110°C in a sealed tube for 18 h. The resulting black solution was evaporated under reduced pressure and purified by flash chromatography (eluent pentane/0.5% triethylamine) to give the vinylsilane (0.52 g, 80%) as a mixture of $E:Z$ isomers. IR (neat 1625 cm^{-1} (υC=C); ^{19}F NMR ($CDCl_3$) δ −64.0; −67.6, ^1H NMR ($CDCl_3$) δ 0 (s, 9H), 1.7 (m 2H), 2.2 (m, 2H), 2.5 (m, 2H), 5.8 (s, 0.5H), 6.05 (s, 0.5H), 7.1 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.2/0.5, 29.9/30.3, 31.5/33.5, 35.3/36.1, 122.3 (q J_{CF} = 280.0Hz), 126.3, 128.4, 133.6/136.4, 141.5/141.8, 144.0 (q, J_{CF} = 35.2Hz), Anal. Calc. for $C_{15}H_{21}F_3Si$: C 62.8, H 7.3; Found C 62.9, H 7.3%.
[15] New compounds were characterised by IR, ^{19}F NMR, ^1H NMR, and ^{13}C NMR spectroscopy, and elemental analysis.
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