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Extremely facile formation and high reactivity of new thioacylsilanes containing the ferrocene moiety

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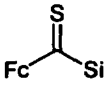
Abstract

Thioacylsilanes containing the ferrocene moiety, easily prepared from the corresponding acylsilanes with Lawesson's reagent at room temperature, can be transformed into vinyl silanes, sulfur heterocycles and sulfines.

Keywords: ferrocene derivatives; thioacylsilanes; acylsilanes; vinylsilanes.

Ferrocene derivatives have attracted increasing attention owing to their potential in various fields such as homogeneous catalysis, organic synthesis and material chemistry.[1] As a part of our general interest in the chemistry of thioacylsilanes used as intermediates for the synthesis of a large variety of compounds containing the Si–C–S unit[2] and as equivalents of unstable thioaldehydes,[3] we report here an extremely facile formation of thioacylsilanes **1a–c** containing the ferrocene moiety and their conversion into vinyl silanes, sulfur heterocycles and sulfines.



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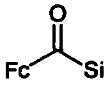

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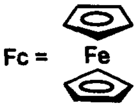

a: Si = $SiMe_3$
b: Si = $SiMe_2Ph$
c: Si = $SiPh_3$

Thioacylsilanes are obtained by thionation of the corresponding acylsilanes.[2] The synthesis of the acylsilanes **2a–c** reported in the literature consists in a four-step sequence starting from formyl ferrocene using the dithiane hydrolysis route.[4,5] We prepared the acylsilanes **2a–c** in a more straight way by nucleophilic silylation of ferrocenecarboxylic acid chloride **3** which in turn was obtained[6] from the commercially available carboxylic acid. This methodology already reported for the synthesis of trimethylsilyl,[7] dimethylphenylsilyl[8] and triphenylsilyl[9] derivatives, gave a very good yield of acylsilanes **2a–c** (Scheme 1).

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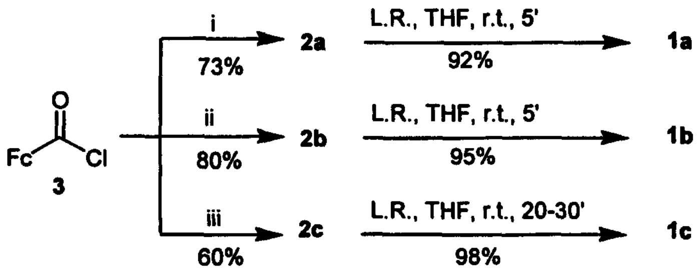
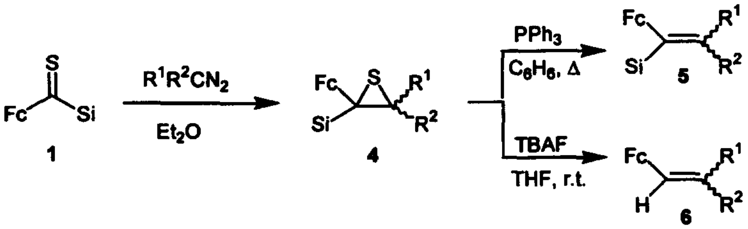
The transformation of **2a–c** into **1a–c** was accomplished with the Lawesson's reagent in THF and it occurs in excellent yields at room temperature in a few minutes (Scheme 1), whereas the thionation of ketones[10] and of other acylsilanes,[3] with the same reagent, is normally performed at high temperature. Products **1a–c** were purified by chromatography on florisil and gave correct elemental and spectroscopic analysis.[11]



Scheme 1. (i) $(Me_3Si)_2$ (14.4 mmol), MeLi (12 mmol), CuCN (6 mmol), THF, HMPA (6 ml), –30°C; (ii) $PhMe_2SiLi$ (20 mmol), CuCN (10 mmol), THF, –78→0°C; (iii) Ph_3SiLi (10 mmol), CuI (10 mmol), THF, –50°C

The reaction of **1a,b** with ethyl diazoacetate, performed both at 0 and 15°C, gave the thiiranes **4a,b** in good to very good yields (Table 1). On the contrary, Huisgen et al.[12] have shown that the reaction of thiobenzophenone with methyl diazoacetate affords a mixture of two isomeric 1,3-dithiolanes. The stereochemistry of the adducts **4a** and **4b** was assigned with the aid of NOE technique on the crude reaction mixture.[13] The *Z*/*E* ratio was determined by integration of the signals (^{1}H NMR) of the silyl and the CH groups. Reaction of **1b** with diphenyl diazomethane gave similarly the tetrasubstituted thiirane **4c**.

Table 1

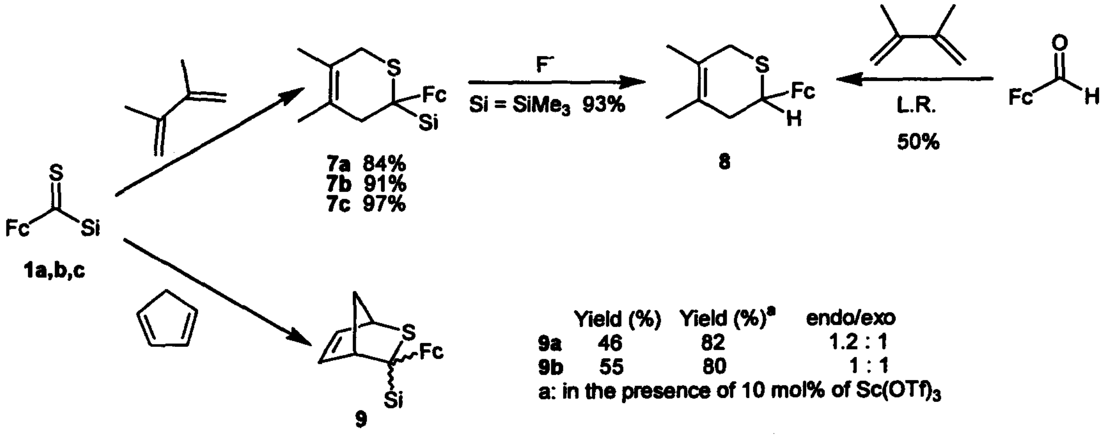


Si	R^1	R^2	T (°C)	4	(%)	*Z*:*E*	5	(%)	*Z*/*E*	6	(%)	*Z*:*E*
$SiMe_3$	H	CO_2Et	0	a	67	2.4:1	a	59	2.4:1			
$SiMe_3$	H	CO_2Et	15	a	55	1.6:1	a	60	1.8:1			
$SiMe_2Ph$	H	CO_2Et	0	b	94	2.6:1	b	60	2.5:1			
$SiMe_2Ph$	H	CO_2Et	15	b	84	2.6:1	b	65	2.6:1			
$SiMe_3$	H	CO_2Et	15	a	60	1.6:1				a	90	2.5:1
$SiMe_2Ph$	H	CO_2Et	15	b	83	2.6:1				b	89	4.5:1
$SiMe_2Ph$	Ph	Ph	20	c	86	-	c	84	-			

The desulfurization of **4a–c**, performed with triphenylphosphine was stereospecific, within the experimental errors, giving the corresponding vinyl silanes **5a–c**[14] in good yields (Table 1).

Treatment of **4a,b** with a solution of TBAF in THF at room temperature gave olefins **6a,b**[15] as the result of a concomitant desilylation and desulfurization. It is most likely that the first step of this reaction is the desulfurization via the intermediacy of difluoro sulfurane, a species that is known for the alkyl and the aryl sulfides.[16] In fact, performing the same reactions in heterogeneous conditions with CsF in CH_3CN, we obtained vinyl silanes **5a,b** in moderate yields and with the prevalent formation of the *Z* isomers. It is well known[17] that CsF in aprotic media is less active that the tetraalkylammonium derivative.

The cycloaddition of **1a–c** with 2,3-dimethylbuta-1,3-diene afforded products **7a–c**[18] in excellent yields. The protiodesilylation performed on **7a** using tetrabutylammonium fluoride (TBAF) in THF at room temperature gave product **8** in 93% yield, whereas the cycloaddition of the in situ generated thioformyl ferrocene and 2,3-dimethylbuta-1,3-diene in boiling THF gave **8** in only 50% yield. Cycloaddition of **1a,b** with cyclopentadiene gave the adducts **9a,b** in moderate yields. Better yields of **9a,b** were obtained when the reaction was performed in the presence of catalytic amounts of $Sc(OTf)_3$. In both cases no significant diastereoselectivity has been observed (Scheme 2).

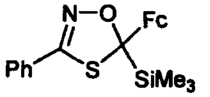


	Yield (%)	Yield (%)[a]	endo/exo
9a	46	82	1.2 : 1
9b	55	80	1 : 1

a: in the presence of 10 mol% of $Sc(OTf)_3$

Scheme 2.

The reaction of **1a** with benzonitriloxide, produced in situ from benzohydroximoyl chloride and Et_3N occurred smoothly at room temperature to afford the cycloadduct **10** in 67% yield. The regiochemistry of the reaction was assigned through the protiodesilylation with fluoride ion, which underwent an easy ring fragmentation[19] to $(FcCOS)_2$,[20] benzonitrile and Me_3SiOH. Oxidation of **1b** with *m*-CPBA gave the corresponding thioacylsilane *S*-oxide **11**[21] to which we tentatively assigned the *E* configuration on the basis of the deshielding effect of the CSO group.[22]



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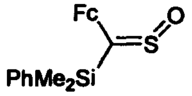

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In conclusion the presence of the ferrocene moiety into acylsilanes highly increases the ease of transformation of the C=O into the C=S group. Moreover many molecules containing ferrocene, sulfur and silicon can be synthesized due to the high reactivity of thioacylsilanes. Further studies are in progress on achiral and chiral derivatives.

Acknowledgements

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11. Selected data for **1a–c**: **1a**: IR (CCl_4) ν_{max}, cm^{-1}: 1250 (CS); ^1H NMR (300 MHz) δ, ppm: 0.366 (9H, s, $SiMe_3$), 4.14 (5H, s, Fc-H), 4.81 (2H, t, J=1.98 Hz, Fc-H), 5.06 (2H, t, J=1.98 Hz, Fc-H); ^{13}C NMR (75.46 MHz) δ, ppm: 1.13 ($SiMe_3$), 69.96, 71.20, 74.44 (Fc-CH), 95.14 (Fc-C), 284.10 (CS); MS (*m/z*): 302 (M^+), 73 ($SiMe_3$).
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13. Selected data for **4a,b**: **4b**: IR (CCl_4) ν_{max}, cm^{-1}: 1710 (CO_2Et); ^1H NMR (300 MHz) δ, ppm: 0.265, 0.340 (6H, s, $SiMe_2$, *Z* isomer), 0.398, 0.517 (6H, s, $SiMe_2$, *E* isomer), 1.26 (3H, t, J=6.9 Hz, CH_3, *E* isomer), 1.27 (3H, t, J=6.8 Hz, CH_3, *Z* isomer), 3.49 (1H, bs, CH, *E* isomer), 3.62 (1H, bs, CH, *Z* isomer), 3.90–4.30 (22H, m, 18Fc-H, $2CH_2$), 7.22–7.41 (8H, m, Ar-H), 7.61 (2H, m, Ar-H); MS (*m/z*): 418 (M^+–S), 364 ((M^+–S)–$CHCO_2Et$), 135 ($SiMe_2Ph$). Irradiation of the $SiMe_2$ groups signals at 0.398 and 0.517 ppm produced a significant increase (11%) in the intensity of the CH signal of the *E* isomer at 3.49 ppm.
14. Selected data for **5a,b**: (*Z*)-**5a** and (*E*)-**5a** were separated by chromatography on silica (15:1 light petroleum:diethyl ether) of the crude reaction mixture: (*Z*)-**5a**: IR (CCl_4) ν_{max}, cm^{-1}: 1720 (CO_2Et); ^1H NMR (300 MHz) δ, ppm: 0.196 (9H, s, $SiMe_3$), 1.31 (3H, t, J=7.2 Hz, CH_3), 4.12 (5H, s, Fc-H), 4.18 (2H, q, J=7.2 Hz, CH_2), 4.22 (4H, bs, Fc-H), 6.87 (1H, s, CH=); ^{13}C NMR (75.46 MHz) δ, ppm: 0.829 ($SiMe_3$), 14.351 (CH_3), 60.203 (CH_2), 68.290, 69.065, 69.455 (Fc-CH), 91.400 (Fc-C), 131.511 (CH=), 162.088 (C=), 167.247 (C=O); MS (*m/z*): 356 (M^+), 341 (M^+–CH_3), 328 (M^+–C_2H_4), 312 (M^+–C_2H_4O), 291 (M^+–C_6H_5), 73 ($SiMe_3$). (*E*)-**5a**: IR (CCl_4) ν_{max}, cm^{-1}: 1720 (CO_2Et); ^1H NMR (300 MHz) δ, ppm: 0.273 (9H, s, $SiMe_3$), 1.31 (3H, t, J=7.1 Hz, CH_3), 4.07 (5H, s, Fc-H), 4.21 (2H, q, J=7.1 Hz, CH_2), 4.28 (2H, dd, J_1=J_2=1.9 Hz, Fc-H), 4.58 (2H, dd, J_1=J_2=1.9 Hz, Fc-H), 6.18 (1H, s, CH=); ^{13}C NMR (75.46 MHz) δ, ppm: –0.327 ($SiMe_3$), 14.286 (CH_3), 60.194 (CH_2), 69.115, 69.620, 70.438 (Fc-CH), 81.518 (Fc-C), 125.127 (CH=), 153.008 (C=), 167.763 (C=O); MS (*m/z*): 356 (M^+), 341 (M^+–CH_3), 328 (M^+–C_2H_4), 312 (M^+–C_2H_4O), 291 (M^+–C_6H_5), 73 ($SiMe_3$). The configuration of the double bond of (*Z*)-**5a** and (*E*)-**5a** was elucidated by NOE experiments performed on the mixture of the two isomers: saturation of the $SiMe_3$ groups resonance at 0.196 and 0.273 ppm produced a significant increase (14%) in the intensity of the vinylic proton signal of the *E* isomer at 6.18 ppm.
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18. Selected data for **7a–c**: **7a**: ^1H NMR (300 MHz) δ, ppm: –0.175 (9H, s, $SiMe_3$), 1.73 (3H, s, CH_3), 1.77 (3H, s, CH_3), 2.38 (1H, d, J=1.6 Hz, CH), 2.75 (1H, d, J=16 Hz, CH), 2.95 (1H, d, J=16 Hz, CH), 3.21 (1H, d, J=16 Hz, CH), 3.92 (1H, bs, Fc-H), 4.05 (1H, bs, Fc-H), 4.10 (1H, bs, Fc-H), 4.12 (1H, bs, Fc-H), 4.20 (5H, bs, Fc-H); ^{13}C NMR (75.46 MHz) δ, ppm: –1.98 ($SiMe_3$), 19.51, 20.90 (CH_3), 31.09, 39.60 (CH_2), 65.92, 65.95, 66.10, 66.48, 68.58 (Fc-CH), 97.04 (Fc-C), 123.90, 126.80 (C=).
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21. Compound **11**: IR (CCl_4) ν_{max}, cm^{-1}: 1110 (CSO); ^1H NMR (300 MHz) δ, ppm: 0.6 (6H, s, $SiMe_2$), 3.95 (5H, s, Fc-H), 4.4 (2H, t, J=1.8 Hz, Fc-H), 5.05 (2H, t, J=1.8 Hz, Fc-H), 7.4 (3H, m, Ar-H), 7.6 (2H, m, Ar-H); ^{13}C NMR (75.46 MHz) δ, ppm: –1.6 ($SiMe_2$), 69.49, 70.54, 70.67, 70.99 (Fc-CH), 78.9 (Fc-C), 128.2, 130.04, 133.91 (Ar-CH), 135.35 (Ar-C), 186.68 (CSO); MS (*m/z*): 380 (M^+), 348 (M^+–S), 135 ($SiMe_2Ph$).
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