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Synthesis and Structure of O-silylated 2-Polyfluoroacyl-cycloalkanones

Dmitri V. Sevenard* and **Gerd-Volker Röschenthaler**

Institute of Inorganic and Physical Chemistry, University of Bremen, D-28334 Bremen, Germany

Summary. 2-Acyl-cycloalkanones containing polyfluoroalkyl groups react with dichlorodimethylsilane to form the corresponding heterocyclic *bis*-enol derivatives. The reaction of 2-polyfluoroacyl-cycloalkanones with chlorotrimethylsilane leads to mixtures of the corresponding (*Z*)-configured O-silylethers. The silatropy process in this case is slow on the NMR time scale.

Keywords. Chlorosilanes; Enoles; 2-Polyfluoroacyl-cycloalkanones; Silyl ethers; Tautomerism.

Introduction

O-Silylated derivatives of 1,3-diketones are an important class of precursors in heteroatom chemistry [1–5]. One of the possible 1,3-diketone tautomeric forms is fixed in these compounds which have been obtained reacting 1,3-dicarbonyls with chlorosilanes. Thus, the reaction of 2-acetyl-cycloalkanones with dichlorosilanes R_2SiCl_2 ($R = Me$, Ph) has afforded heterocycles with a *bis*-enol structure [6]. Such silyl ethers are not simply the substitution products of the precursor diketones; for example, 1,1,1,5,5,5-hexafluoroacetylacetone exists as a (*Z*)-enol stabilized by hydrogen bonding, whereas the O-trimethylsilyl substituted derivative is (*E*)-configured [7], resulting in different chemical properties [2–4]. (*Z*)-Configurated silyl ethers of 1,3-diketones equilibrate fast and are indistinguishable by GLC and NMR spectroscopy at room temperature [1, 7, 8]. The transformation of (*Z*)-forms has been considered either as a 1,5-sigmatropic rearrangement [1] or as an internal nucleophilic displacement [7, 8].

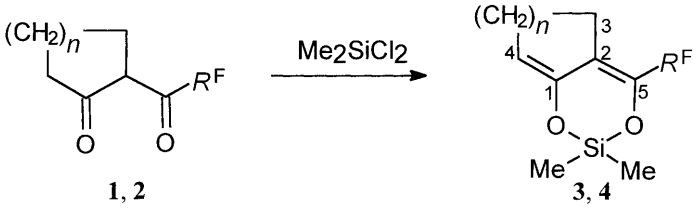
We report here the synthesis and structure of O-silyl ethers of 2-polyfluoroacyl-cycloalkanones as a part of our systematic investigation of this class of compounds.

Results and Discussion

We found that 1,3-diketones **1** and **2** react with dichlorodimethylsilane in the presence of a twofold excess triethylamine to furnish the cyclic *bis*-enol derivatives **3** and **4** in 63 and 77% yield (Scheme 1).

In the ^{13}C NMR spectra of **3** and **4** (Table 1), through-space coupling of C^3 with fluorine ($^4J_{C-F}$) was observed. An interesting feature was displayed by the carbon

* Corresponding author. E-mail: sevenard@chemie.uni-bremen.de



1, 2 **3, 4**

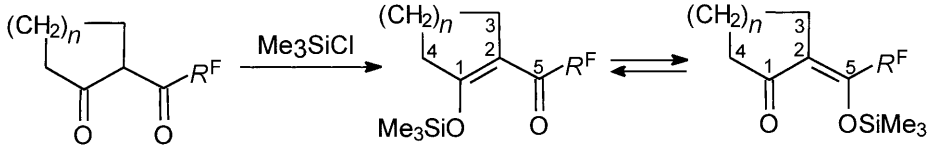
	n	R^F
1, 3	1	C_3F_7
2, 4	2	CF_3

Scheme 1

nuclei of the 1,3-diene system: there is not only a triplet or quartet splitting for C^5 ($^2J_{C-F}$) and C^2 ($^3J_{C-F}$), but also for C^1 ($^4J_{C-F}$) and, unexpectedly, for C^4 ($^5J_{C-F}$). Moreover, in the ^1H NMR spectrum of **4** (Table 2) further fine structure was detected for the olefinic triplet – its single components consist of badly resolved quartets ($^6J_{H-F} = ca.$ 0.6 Hz). Probably, the presence of conjugated C–C double bonds and the favourable W-arrangement of nuclei is responsible for the effective through-bond spin information transmission between C or H and F.

When 2-polyfluoroacyl-cycloalkanones **1**, **2**, and **5** were allowed to react with *TMS*Cl in the presence of triethylamine, the O-silyl ethers **6–8** were formed as yellowish moisture sensitive liquids in 63–79% yields (Scheme 2).

Compounds **6–8** exist in $CDCl_3$ solution as an equilibrium mixture of *endo*- and *exo*-enol forms **A** and **B** (Scheme 2). The rapid rearrangement between the (*Z*)-enol forms of silylated unsymmetrical 1,3-diketones at room temperature resulting in only one average set of signals in the respective NMR spectra has been the subject of earlier reports [1, 7]. However, for compounds **6–8**, separate signals of forms **A** and **B** could be observed at 25°C in $CDCl_3$. The ratio of tautomers in these mixture was determined by the integral intensities of the corresponding signals in the ^1H and



1, 2, 5 **A** **6-8** **B**

	n	R^F	**A**:**B**
1, 6	1	C_3F_7	32:68
2, 7	2	CF_3	90:10
5, 8	1	CF_3	60:40

Scheme 2

Table 1. ^{13}C NMR data of compounds **3** and **4** (δ/ppm, J/Hz)

	Me	$(CH_2)_n$	C^3	C^2	C^4	R^F	C^5	C^1
3	−2.1	26.4	24.4 (t, $^4J_{C-F} = 3.8$)	112.3 (t, $^3J_{C-F} = 1.9$)	126.2 (t, $^5J_{C-F} = 2.6$)	109.7 (tq, $^1J_{C-F} = 266.0$, $^2J_{C-F} = 37.7$) 112.6 (tt, $^1J_{C-F} = 255.8$, $^2J_{C-F} = 30.5$) 118.3 (qt, $^1J_{C-F} = 287.1$, $^2J_{C-F} = 34.3$)	128.8 (t, $^2J_{C-F} = 29.0$)	149.8 (t, $^4J_{C-F} = 1.9$)
4	−1.5	22.7, 24.3	24.7 (q, $^4J_{C-F} = 2.8$)	111.2 (q, $^3J_{C-F} = 1.1$)	115.0 (q, $^5J_{C-F} = 2.8$)	121.5 (q, $^1J_{C-F} = 274.2$)	133.3 (q, $^2J_{C-F} = 34.8$)	144.4 (s)

Table 2. ^1H and ^{19}F NMR data of compounds **3** and **4** (δ/ppm, J/Hz)

	^1H			^{19}F
	Me	$(CH_2)_{n+1}$	=CH	
3	0.35	2.37–2.41, 2.69–2.79 (two m)	5.23 (t, $^3J_{H-H} = 2.9$)	−128.8 (br s, CF_2) −118.34 (m, CF_2) −82.55 (t, CF_3, $^4J_{F-F} = 8.6$)
4	0.34	1.60–1.75, 2.12–2.21, 2.42–2.52 (three m)	5.28 (tq, $^3J_{H-H} = 4.6$, $^6J_{H-F} \approx 0.6$)	−65.87 (s)

^{19}F NMR spectra. The equilibrium depends not only strongly on the size of the 1,3-diketone carbocycle, but also on the chain length of the polyfluoroalkyl group.

The NMR spectra (Tables 3–5) of **6–8** show two sets of signals. The structure determination of the coexisting isomeric forms **A** and **B** could be achieved by ^{13}C NMR spectroscopy (Table 5). The δ_C values of C^2 in both sets (111.8–128.5 ppm) represent unequivocally their olefinic character, excluding the C-silylated isomer. The assignments for C^{CO} (C^1 and C^5) could be performed *via* their $^2J_{C-F}$ coupling. The respective δ_C values of form **B** differ very strongly ($\Delta\delta(C^1\text{-}C^5) = ca.$ 64 ppm), the signal of the the polyfluoroacyl keto carbon C^5 appearing at higher field (137.5–141.8 ppm). The shielding of the carbonyl carbon nuclei increases substantially upon enolization [9], referring to an *exo*-enol structure for **B**. The magnitude of $^1J_{C-F}$ in the trifluoromethylated compounds **7** and **8** differs markedly for the two coexisting forms; for **B**, $^1J_{C-F} = 277.6$ (**7**) and 278.0 (**8**) Hz was observed (analogously to the *exo*-enol compound **4** with $^1J_{C-F} = 274.2$ Hz). The *exo*-enol structure of form **B** in **7** is additionally confirmed by a quartet splitting ($^5J_{C-F} = 0.8$ Hz) found for the carbons of Me_3Si. The C^3 signal exhibits a fine structure resulting from a $^4J_{C-F}$ coupling, an unequivocal proof for the (*Z*)-configuration of the exocyclic C–C double bond [10, 11].

In form **A**, the signals of C^{CO} are in a similar region ($\Delta\delta(C^1\text{-}C^5) =$ 3.7–13.9 ppm). For the CF_3 group, $^1J_{C-F}$ values of 289.2 (**7**) and 289.4 (**8**) Hz were found. For compounds containing trifluoroacetyl groups in conjugation with a fixed *endo*-enol fragment a coupling constant of $^1J_{C-F} = 289.2$ Hz has been

Table 3. ^{1}H NMR data of compounds **6–8** (δ/ppm, J/Hz)

	endo-enol form (**A**)		*exo*-enol form (**B**)	
	Me	$(CH_2)_{n+2}$	Me	$(CH_2)_{n+2}$
6[a]	0.26	1.78–1.97 (m, CH_2), 2.40–2.67 (m, 2 CH_2)	0.23	1.78–1.97, 2.73–2.86 (two m) 2.27 (t, CH_2, $^3J_{H-H} = 7.8$)
7[b]	0.23	1.49–1.72 (m, 2 CH_2) 2.27 (t, 2 CH_2, $^3J_{H-H} = 5.5$)	0.19	1.65–1.93, 2.39–2.50 (two m)
8[c]	0.17	1.71–1.85 (m, CH_2), 2.47 (t, CH_2, $^3J_{H-H} = 7.6$) 2.59–2.76 (m, CH_2)	0.13	1.71–1.85 (m, CH_2) 2.16 (t, CH_2, $^3J_{H-H} = 7.7$) 2.47 (t, CH_2, $^3J_{H-H} = 7.6$)

[a] **A**:**B** = 33:67; [b] **A**:**B** = 90:10; [c] **A**:**B** = 60:40

Table 4. ^{19}F NMR data of compounds **6–8** (δ/ppm, J/Hz)

	endo-enol form (**A**)	*exo*-enol form (**B**)
6[a]	−127.37 (s, CF_2)	−128.11 (s, CF_2)
	−119.16 (q, CF_2, $^4J_{F-F} = 8.6$)	−116.43 (q, CF_2, $^4J_{F-F} = 5.2$)
	−81.60 (m, CF_3)	−82.30 (m, CF_3)
7[b]	−75.58 (s)	−66.54 (s)
8[c]	−77.33 (s)	−70.48 (s)

[a] **A**:**B** = 31:69; [b] **A**:**B** = 90:10; [c] **A**:**B** = 60:40

Table 5. ^{13}C NMR data of compounds **6–8** (δ/ppm, J/Hz)

	Me	C^3	$(CH_2)_n$	C^4	C^2	R^F	C^1	C^5
6[a]	0.2 (s)	28.6 (s)[c]	19.5 (s)	36.6 (s)	113.6 (s)	109.0–117.8 (m s)	172.4	178.7 (t, $^2J_{C-F} = 27.3$)
7[a]	0.6 (s)	21.6, 22.2, 24.1 (three s)		32.3 (s)	111.8 (s)	116.7 (q, $^1J_{C-F} = 289.2$)	166.7	180.6 (q, $^2J_{C-F} = 35.5$)
8[a]	−0.2 (s)	27.9 (s)	19.6 (s)	36.2 (s)	111.9 (s)	116.4 (q, $^1J_{C-F} = 289.4$)	171.8	175.5 (q, $^2J_{C-F} = 36.4$)
6[b]	0.2 (s)	27.0 (t, $^4J_{C-F} = 5.5$)	19.9 (t, $^5J_{C-F} = 1.9$)	39.0 (s)	122.9 (s)	109.0 (tq, $^1J_{C-F} = 266.4$, $^2J_{C-F} = 38.1$) 112.1 (tt, $^1J_{C-F} = 259.2$, $^2J_{C-F} = 31.8$) 117.7 (qt, $^1J_{C-F} = 287.8$, $^2J_{C-F} = 33.9$)	205.0	141.8 (t, $^2J_{C-F} = 26.4$)
7[b]	−0.2 (q, $^5J_{C-F} = 0.8$)	24.9 (q, $^4J_{C-F} = 0.8$)	26.4, 29.6 (two s)	43.2 (s)	128.5 (q, $^3J_{C-F} = 2.3$)	120.1 (q, $^1J_{C-F} = 277.6$)	201.9	137.5 (q, $^2J_{C-F} = 36.6$)
8[b]	−0.4 (s)	26.4 (q, $^4J_{C-F} = 2.7$)	19.5 (s)	38.9 (s)	120.0 (q, $^3J_{C-F} = 1.8$)	120.1 (q, $^1J_{C-F} = 278.0$)	204.7	141.2 (q, $^2J_{C-F} = 35.5$)

[a] *endo*-enol form **A**; [b] *exo*-enol form **B**; [c] broad signal, probably due to unresolved $^4J_{C-F}$

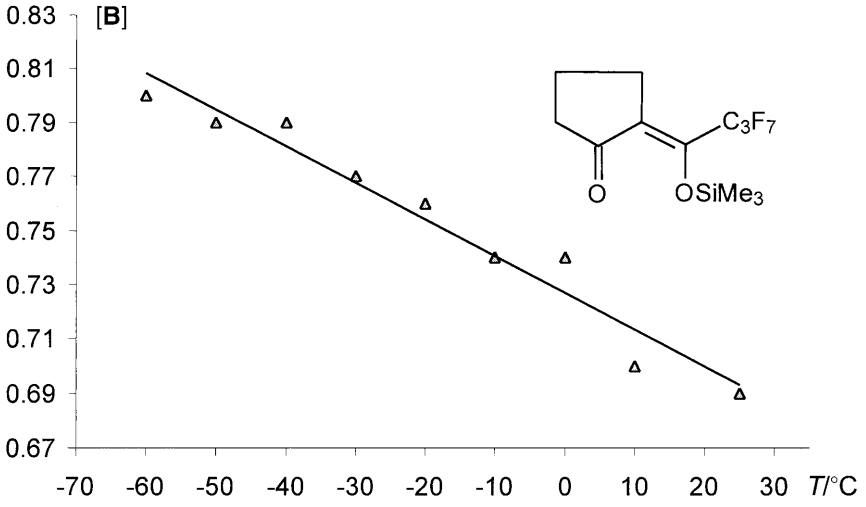


Fig. 1. Temperature dependence of the molar concentration of form **B** of compound **6** (from ^{19}F NMR data); $\Delta H^{\circ}_{\mathbf{A-B}} = -3685 \pm 324\,\mathrm{J/mol}$, $\Delta S^{\circ}_{\mathbf{A-B}} = -6.22 \pm 1.48\,\mathrm{eu}$

observed [12]. These arguments account for the *endo*-enol structure of **A** (cf. Ref. [13]). In the case of a third possible form with (*E*)-configuration of the *exo*-C-C-double bond, the shifts of the carbonyl carbons would obviously be similar to those in form **B** and should show considerably larger $\Delta\delta_C$ values, an additional argument for the *endo*-structure of the second form.

In the ^{1}H NMR spectra (Table 3) the Me_3Si signals of **A** und **B** are distinctly separated. The respective signal of the *exo*-form **B** is shifted for all three compounds to higher field compared to *endo*-form **A**.

The ^{19}F NMR spectra of the CF_3 substituted compounds **7** and **8** (Table 4) show the *endo*-enol **A** singulet at higher field than in the *exo*-enol **B** ($\delta_F = -75.58$ and -66.54 (**7**), -77.33 and -70.48 (**8**) ppm). The CF_3 signal of the *exo*-enol **B** in **7** was observed in the same region as the corresponding resonance of the related compound **4** with a fixed *exo*-enol fragment ($\delta_F = -66.54$ *vs.* -65.87 ppm), which is in good agreement with the signal assignment.

Low temperature ^{19}F NMR measurements of **6** prove the presence of the equilibrium **A**⇄**B**. With increasing concentration of **B** that of **A** decreases (Fig. 1), thus confirming the structure of the coexisting isomers (the (*E*)-*exo*-enol form is unable to be converted into the other forms [7]).

In conclusion, 2-polyfluoroacyl cycloalkanones act as O-nucleophiles in reactions with Si-electrophiles. For monosilylated derivatives of 2-polyfluoroacyl-cycloalkanones (unlike for linear CF_3-1,3-diketones), the silatropy process in $CDCl_3$ is slow on the NMR time scale.

Experimental

General

Boiling points are uncorrected. Mass spectra (EI, 70 eV) were measured on a MAT 8200 spectrometer. NMR spectra (standards: *TMS* (^{1}H, ^{13}C), $CFCl_3$(^{19}F)) were recorded as 50% $CDCl_3$

solutions on a Bruker DPX-200 spectrometer operating at 200.1 (^{1}H), 50.3 (^{13}C), and 188.3 (^{19}F) MHz. 2-Polyfluoroacyl-cycloalkanones **1** [14], **2** [15, 16] and **5** [15] were prepared by a *Claisen*-type condensation of cyclopentanone or cyclohexanone and alkylpolyfluoroacylates in the presence of sodium methylate in dry ether [15, 16].

General method for the synthesis of compounds **3** *and* **4**

To a solution of 52 mmol 1,3-diketone and 100 mmol dry triethylamine (10.4 g) in 100 cm^3 dry diethyl ether, a solution of 52 mmol (6.7 g) freshly distilled dichlorodimethylsilane in 20 cm^3 dry diethyl ether was added within 0.5 h. After stirring for 16 h, triethylamine hydrochloride was filtered off and washed with cold diethyl ether (2×10 cm^3). The solvent was removed, and the residue was distilled *in vacuo*.

7-Perfluoropropyl-1,2-dihydro-5,5-dimethyl-4,6-dioxa-5-silaindene (**3**; $C_{11}H_{11}F_7O_2Si$)

Yellow oil; yield: 63%; b.p.: 94–96°C (20 torr); MS: *m/z* (%) = 336 (M^+, 100), ($[M\text{-}C_2F_5]^+$, 72), 167 ($[M\text{-}C_3F_7]^+$, 38), and other fragments; HRMS: found 336.0409, calcd. 336.0417.

4-Trifluoromethyl-6,7-dihydro-2,2-dimethyl-5H-1,3-dioxa-2-silanaphthalene (**4**; $C_{10}H_{13}F_3O_2Si$)

Colorless liquid; yield: 77%; b.p.: 48–51°C (0.8 torr, first distillation), 41–44°C (0.9 torr, second distillation); MS: *m/z* (%) = 250 (M^+, 100), 235 ($[M\text{-}Me]^+$, 62), 181 ($[M\text{-}CF_3]^+$, 70), 166 ($[M\text{-}Me\text{-}CF_3]^+$, 10), and other fragments; HRMS: found: 250.0633, calcd. 250.0637.

General method for the synthesis of compounds **6–8**

To a solution of 8 mmol 1,3-diketone and 8 mmol (0.8 g) dry triethylamine in 10 cm^3 dry diethyl ether, a solution of 8 mmol (0.9 g) freshly distilled chlorotrimethylsilane in 5 cm^3 dry diethyl ether was added within 0.5 h. After stirring for 0.5 h, triethylamine hydrochloride was filtered off and washed with cold diethyl ether (2×5 cm^3). The solvent was removed, and the residue was distilled *in vacuo*. The products are yellowish liquids (compound **8** could not be isolated in pure state, but was characterized by MS and NMR spectroscopy).

2-Perfluorobutanoyl-1-trimethylsiloxycyclopentene (**6**; $C_{12}H_{15}F_7O_2Si$)

Yield: 79%; b.p.: 52–55°C (1 torr); MS: *m/z* (%) = 352 (M^+, 13), 337 ($[M\text{-}Me]^+$, 100), 183 ($[M\text{-}C_3F_7]^+$, 45), 73 (Me_3Si^+, 21), 15 (Me^+, 10), and other fragments; HRMS: found 352.0720, calcd. 352.0730.

2-Trifluoroacetyl-1-trimethylsiloxycyclohexene (**7**; $C_{11}H_{17}F_3O_2Si$)

Yield: 63%; b.p.: 114–116°C (10 torr); MS: *m/z* (%) = 266 (M^+, 18), 251 ($[M\text{-}Me]^+$, 70), 197 ($[M\text{-}CF_3]^+$, 100), 169 ($[M\text{-}CF_3CO]^+$, 6), 97 ($CF_3CO]^+$, 8), 73 (Me_3Si^+, 76), 69 (CF_3^+, 10), and other fragments; HRMS: found 266.0966, calcd. 266.0950.

2-Trifluoroacetyl-1-trimethylsiloxycyclopentene (**8**; $C_{10}H_{15}F_3O_2Si$)

Yield: 74%; b.p.: 50–51°C (1 torr); MS: *m/z* (%) = 252 (M^+, 12), 237 ($[M\text{-}Me]^+$, 100), 183 ($[M\text{-}CF_3]^+$, 32), 73 (Me_3Si^+, 56), and other fragments.

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References

[1] Jullien J, Pechine JM, Perez F, Piade JJ (1982) Tetrahedron **38**: 1413
[2] Francke R, Röschenthaler G-V (1988) Phosphorus, Sulfur, and Silicon **36**: 125
[3] Francke R, Röschenthaler G-V (1989) Z Anorg Allg Chem **572**: 135
[4] Seifert F-U, Röschenthaler G-V (1994) Phosphorus, Sulfur, and Silicon **86**: 157
[5] Schoth R-M, Sevenard D, Pashkevich K, Röschenthaler G-V (2000) Coordination Chem Rev **210**: 101
[6] Cella JA, Mitchell TD (1983) J Organomet Chem **244**: C5
[7] McClarin JA, Schwartz A, Pinnavaia TJ (1980) J Organomet Chem **188**: 129
[8] Howe JJ, Pinnavaia TJ (1969) J Am Chem Soc **91**: 5378
[9] Kol'tsov AI, Ignat'ev Yu A, Kopeykin VV, Panarin EF (1976) Zh Org Khim **12**: 2036
[10] Bouillon J-P, Wynants C, Janousek Z, Viehe HG, Tinant B, Feneau-Dupont J, Declercq JP (1994) Bull Soc Chim Belg **103**: 243
[11] Bouillon JP, Frisque-Hesbain A-M, Janousek Z, Viehe HG (1995) Heterocycles **40**: 661
[12] Sevenard DV, Khomutov OG, Kodess MI, Pashkevich KI, Loop I, Lork E, Röschenthaler G-V (2001) Australian J Chem (in press)
[13] Ebraheem KAK (1991) Monatsh Chem **122**: 157
[14] Trabelsi H, Cambon A (1992) Synthesis 315
[15] Park JD, Brown HA, Lacher JR (1953) J Am Chem Soc **75**: 4753
[16] Lyga JW, Henrie RN, Meier GA, Creekmore RW, Patera RM (1993) Mag Res Chem **31**: 323

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