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Reaction of metal alkoxides with 3-alkyl-substituted acetylacetone derivatives—coordination *vs*. hydrodeacylation

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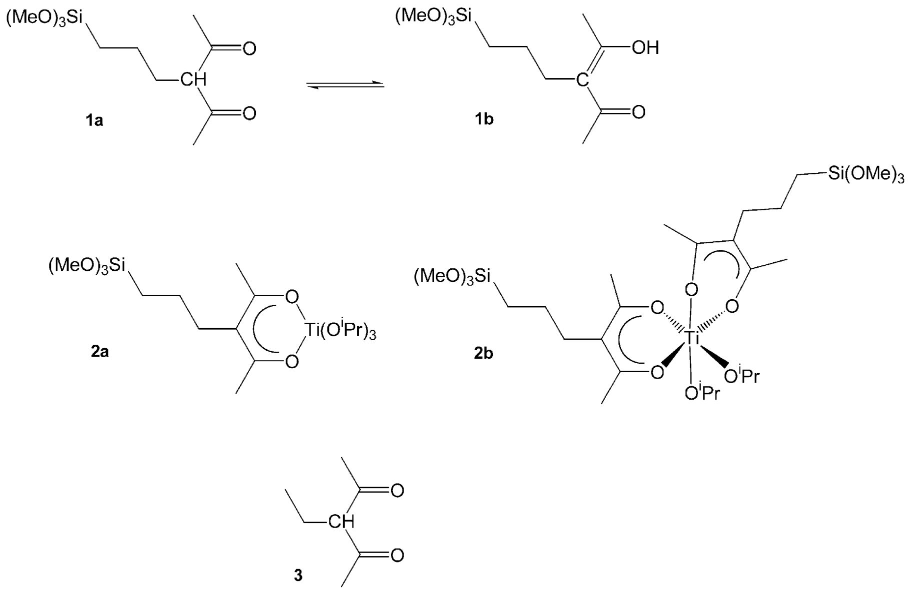
Reaction of $Ti(O^iPr)_4$ or $Zr(OPr)_4$ with 1 or 2 molar equiv of the 3-alkyl-substituted acetylacetone derivatives 3-acetyl-6-trimethoxysilylhexane-2-one or 3-acetylpentane-2-one not only gives the corresponding β-diketonate complexes but also results in about 15% hydrodeacylation of the β-diketone. With the stronger Lewis acid $Al(O^sBu)_3$ hydrodeacylation prevails. Hydrodeacylation is suppressed when a 1 : 5 ratio of metal alkoxide and β-diketone is reacted.

Introduction

Acetylacetone is an often used additive in sol-gel processes to lower the reactivity of metal alkoxides, $M(OR)_x$. Upon reaction with acetylacetone, part of the alkoxide groups is substituted by acetyl acetonate ligands and a new molecular precursor $M(OR)_{x-y}(acac)_y$ (acac = acetyl acetonate) is obtained with a different structure and a lower reactivity towards water. For example, reaction of $Ti(OR)_4$ with acetylacetone, one of the best investigated chemical modification of metal alkoxides, provides dimeric $[Ti(OR)_3(acac)]_2$[1] when a 1 : 1 molar ratio is reacted, and monomeric *cis*-$Ti(OR)_2(acac)_2$ for a 1 : 2 ratio.[2] When the acac derivatives are employed as precursors for sol-gel processing, the OR groups are preferentially hydrolyzed. The same applies to other protic compounds with bi- or multidentate anions.[3]

Besides controlling the reactivity of the metal alkoxides, the bidentate ligands can also be used to introduce functional organic groups into gels.[4] Carboxylates are mainly used for this purpose, while β-diketones with functional organic groups are less often employed. The functional group can be attached at the carbonyl carbon of β-diketones or β-keto esters, as in allyl acetoacetate or 2-(methacryloyloxy)ethyl acetoacetate, or at the carbon between the keto groups (3-R-acac derivatives) as in 3-allyl-2,4-pentanedione,[5,6] a number of bromo-substituted 3-alkylpentanedione derivatives[7] and 3-acetyl-6-trimethoxysilylhexane-2-one (**1**; Scheme 1). Compound **1** was reacted with titanium alkoxides to prepare the new mixed-metal precursors **2a,b**[8] (a monomeric formula is drawn for **2a** in Scheme 1 for simplicity, although the compound should be dimeric—see above), analogous to the $Ti(OR)_{4-x}(acac)_x$ derivatives obtained with unsubstituted acetylacetone. The purpose of preparing the derivatives **2** was to link a $Si(OMe)_3$ and a $Ti(O^iPr)_x$ group by means of the organic spacer and thus to prevent phase separation upon sol-gel processing. Homogeneous gels were indeed obtained, from which anatase and rutile nanocrystals formed upon calcination at unusually high temperatures.[8]

The derivatization of $Ti(OR)_4$ and other metal alkoxides by acetyl acetonate ligands is well-investigated in sol-gel chemistry. Neither complications nor by-products were reported in



Scheme 1

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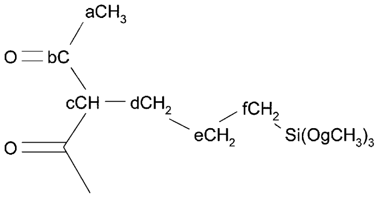
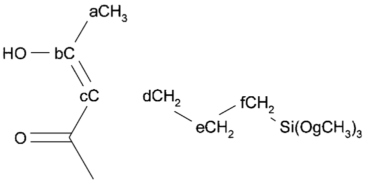
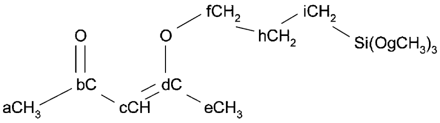
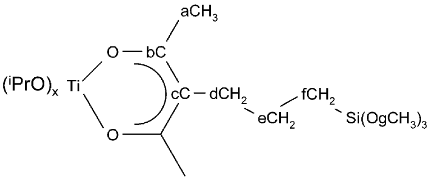
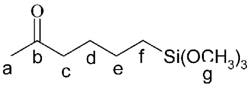
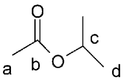
Table 1 ^1H and ^{13}C NMR data of 3-acetyl-6-trimethoxysilylhexane-2-one (**1**) and the O-alkylation by-product **4**, and their assignment. The ratio **1a** : **2a** : **4** was approximately 13 : 5 : 1 [by integration of the **d**CH_2 (**1a**, **1b**) and **f**CH_2 (**4**) signals, respectively].

	^1H δ	^{13}C δ	Assignment[a]
 **1a**	0.67	10.0	m, **f**
	1.35	20.9	m, **e**
	1.85	31.4	q, **d**, $^3J = 7.38$ Hz
	2.16	29.0	s, **a**
	3.64	68.2	t, **c**, $^3J = 6.87$ Hz
	3.55	50.5	**g**
	–	204.3	**b**
 **1b**	0.65	9.1	m, **f**
	1.48	23.7	m, **e**
	2.22	30.6	t, **d**, $^3J = 4.1$ Hz
	2.11	29.0	s, **a**
	–	110.3	**c**
	3.55	50.5	**g**
	–	191.1	**b**
 **4**	0.70	11.0	m, **i**
	1.81	22.1	m, **h**
	2.11	31.6	s, **a**
	2.26	19.4	s, **e**
	3.78	70.0	t, **f**, $^3J = 3.9$ Hz
	3.55	50.5	**g**
	5.48	99.4	m, **c**
	–	171.7	**d**
	–	196.7	**b**

[a] The bold letters refer to the labels in the structural formulas in the left column.

Table 2 ^1H, ^{13}C and ^{29}Si NMR data of the reaction mixture of **1** and $Ti(O^iPr)_4$, and their assignment

	^{29}Si δ	^1H δ	^{13}C δ	Assignment[a]
 **2**	−45.5	0.69	9.9	m, **f**
		1.53	24.1	m, **e**
		2.03	20.3	s, **a**
		2.32	32.3	t, **d**, $^3J = 4.1$ Hz
		3.55	50.5	**g**
		–	113.1	**c**
		–	185.5	**b**
		–	190.8	**h**
 **5**	−47.4	0.60	10.0	m, **f**
		1.40	22.3	m, **e**
		1.55	27.3	m, **d**
		2.11	n. a.	s, **a**
		2.42	43.2	t, **c**, $^3J = 3.6$ Hz
		3.55	50.5	**g**
		–	208.5	**b**
 **6**	—	1.35	21.5	m, **d**
		1.99	21.1	s, **a**
		4.95	67.3	q, **c**, $^3J = 3.2$ Hz
		–	170.1	**b**
Isopropoxy groups	—	1.15	25.2	CH_3
		4.72	77.5	broad, CH
		1.20	25.3	CH_3
		3.98	63.9	quint, $^3J = 3.0$ Hz
		1.23	21.5	CH_3
		4.15	62.7	broad, CH
		1.23	21.5	CH_3
		4.22	65.1	broad, CH

[a] The bold letters refer to the labels in the structural formulas in the left column.

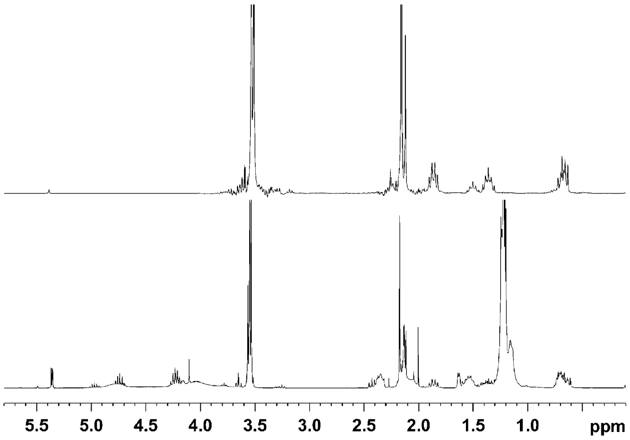
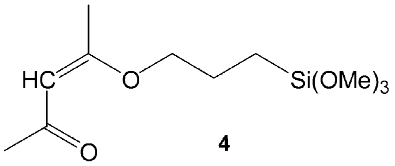


Fig. 1 ^{1}H spectra of **1** (top) and the reaction mixture of Ti(O^{i}Pr)$_4$ with 2 equiv of **1** (bottom) in CDCl$_3$.

the literature. A careful analysis of the NMR and IR spectra of the reaction mixtures of **1** with Ti(O^{i}Pr)$_4$ led us to investigate the reaction of **1**, and 3-acetylpentane-2-one (**3**; Scheme 1) as a simpler model, with Ti(O^{i}Pr)$_4$, Zr(OPr)$_4$ and Al(O^{s}Bu)$_3$ in more detail. We report in this article that the reaction of **1** and **3** is less straightforward than the reactions of unsubstituted acetylacetone, because hydrodeacylation of the 3-substituted β-diketones is competing with the formation of β-diketonate complexes.

Results and discussion

3-Acetyl-6-trimethoxysilylhexane-2-one (**1**) was prepared from iodopropyltrimethoxysilane and acetylacetone by a modification of the previously published procedure.[9] The product contained the O-silylated compound (**4**) as an impurity, which it was not possible to separate from **1**. All proton and carbon signals of the NMR spectra were assigned (Table 1) and served as a reference for the following discussion. The ratio of the keto form (**1a**), the enol form (**1b**) and the O-silylated compound (**4**) was 13 : 5 : 1. This mixture was further used for the following NMR investigations.



4

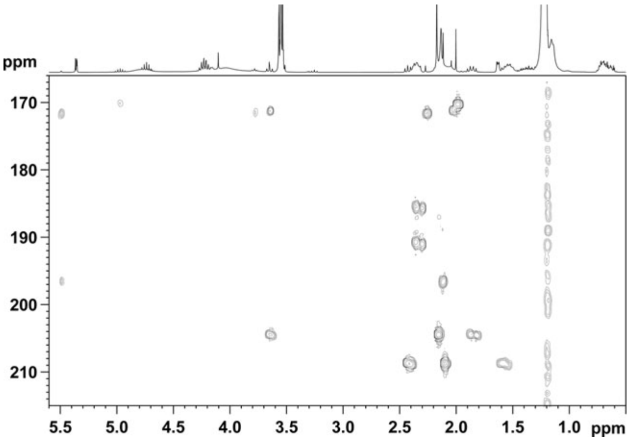


Fig. 2 Section of the HMBC spectrum of Ti(O^{i}Pr)$_4$ with 2 equiv of **1** in CDCl$_3$ (carbonyl region).

The reaction of Ti(O^{i}Pr)$_4$ with 2 equiv of unsubstituted acetylacetone (acac-H) in CDCl$_3$ was performed for comparison. Whereas the ^{13}C NMR spectrum of acetylacetone is characterized by two CO signals at 201.8 ppm for the keto form and 191.1 ppm for the enol form, the ^{13}C NMR spectrum of *cis*-Ti(O^{i}Pr)$_2$(acac)$_2$ showed two signals at 187.1 and 191.2 ppm, due to the stereochemically inequivalent carbon atoms.[10] In the ^{1}H NMR spectrum of Ti(O^{i}Pr)$_2$(acac)$_2$, a singlet at 5.49 ppm was observed for the CH group and two singlets at 1.92 and 2.02 ppm for the two methyl groups. There was no indication for unreacted acetylacetone.

The analogous reaction of Ti(O^{i}Pr)$_4$ with 2 equiv of **1** in CDCl$_3$ led to a rather complicated mixture, whose NMR data are given in Table 2. The ^{1}H spectrum is shown in Fig. 1. Seven different carbonyl signals were observed in the carbonyl region of the ^{13}C NMR spectrum (Fig. 2). Two of them (at 171.7 and 196.7 ppm) were assigned to the O-silylated by-product **4** (see Table 1), two (at 185.5 and 190.8 ppm) to a diketonate complex (**2**) and one (204.3 ppm) to an uncoordinated β-diketone, possibly unreacted **1a** (resonances of the enol form **1b** were not identified). There were two additional carbonyl signals at 170.1 and 208.5 ppm, indicating an ester and a ketone. From the NMR spectra it was not possible to decide whether **2a** or **2b** or both were formed.

The appearance of an ester and a ketone can be explained by a C–C cleavage reaction (hydrodeacylation) of **2** leading to 6-trimethoxysilyl-2-hexanone (**5**) and isopropyl acetate (**6**). The ester **6** was clearly identified by long-range correlation signals in the HMBC spectrum (Fig. 2) of both the isopropyl CH at 4.95 ppm and the CH$_3$ resonance (1.99 ppm) to the corresponding ^{13}C carbonyl signal at 170.1 ppm. The HMBC technique is a sensitive method for the determination of long-range (two- and three-bond) connectivity between ^{1}H and heteronuclei. The ketone **5** was also clearly identified by the corresponding correlation signals in the TOCSY and HMBC spectra. The ^{1}H resonances of the butyl chain were at 0.60, 1.40, 1.55 and 2.42 ppm and both the CH$_3$ resonance at 2.11 ppm and the CH$_2$ resonance at 2.42 ppm showed long-range correlation signals to the carbonyl carbon at 208.6 ppm.

Moreover, an OMe/O^{i}Pr exchange at the silicon atom was observed, the isopropoxy groups originating from Ti(O^{i}Pr)$_4$. The chemical shifts of some isopropoxy groups were indicative of a bridging coordination. The approximate ratio between all reaction products [eqn. (1)] was **5** : **6** : **1a** : **2** = 5 : 5 : 5 : 20 (with **4** still being present), which means that only two thirds of the employed β-diketone **1** was coordinated to titanium.

The reaction of Ti(O^{i}Pr)$_4$ with 1 molar equiv of **1** yielded the same products as in the reaction with 2 equiv. The spectra differed only in the relative concentrations of the products.

Although the initial experiments were carried out with the alkoxysilyl-substituted derivative **1**, we assumed that the observed cleavage reaction is a consequence of the 3-alkyl substituent. We therefore also reacted Ti(O^{i}Pr)$_4$ with 2 equiv of 3-acetylpentane-2-one (**3**; which contained approximately 5% of the O-alkylated compound **7** as a by-product). The reaction mixture was again investigated by NMR spectroscopy (Table 3). The same kinds of products were formed as in the reaction of **1**, that is, the β-diketonate complex(es) **8**, isopropyl acetate (**6**) and 2-pentanone (**9**).

The hydrodeacylation products **5** and **6** were also observed when CD$_2$Cl$_2$, C$_6$D$_6$ or CD$_3$OD were used as the solvent. Reaction of Zr(OPr)$_4$ with 2 molar equiv of **1** in CDCl$_3$ resulted in the same NMR spectra as that of the reaction with Ti(O^{i}Pr)$_4$. When Al(O^{s}Bu)$_3$ was reacted with 1 or 2 equiv of **1**, the hydrodeacylation reaction was nearly quantitative.

Contrary to these findings, *no* hydrodeacylation, that is, only formation of the corresponding β-diketonate complexes, was observed in the NMR spectra when Ti(O^{i}Pr)$_4$, Zr(OPr)$_4$ or Al(O^{s}Bu)$_3$ was reacted with *5* molar equiv of **1**.

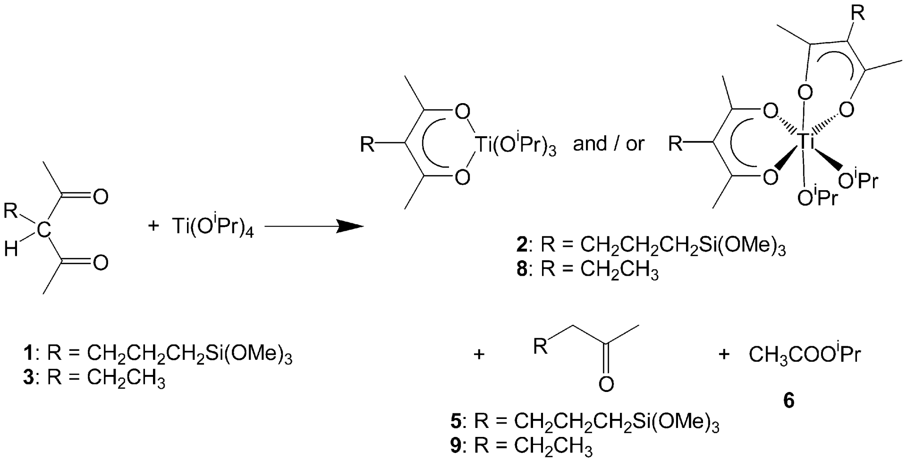
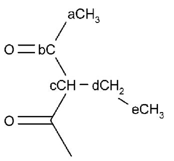
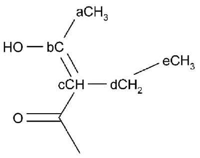
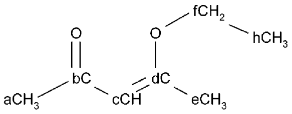
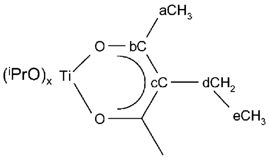
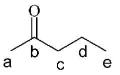
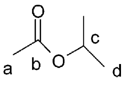
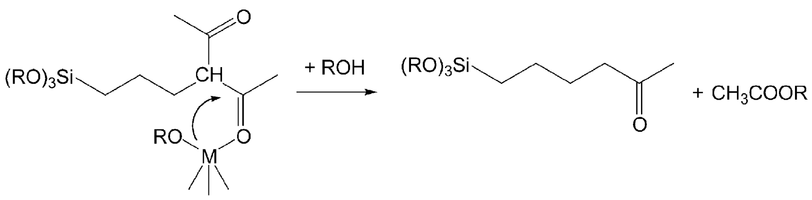


Table 3 ^{1}H and ^{13}C NMR data of the reaction mixture of **3** and Ti(O^{i}Pr)$_4$, and their assignment

	^{1}H δ	^{13}C δ	Assignment[a]
	0.85	11.9	t, **e**, $^3J = 7.46$ Hz
	1.85	21.5	t, **d**, $^3J = 7.37$ Hz
	2.12	29.0	s, **a**
	3.50	70.3	t, **c**, $^3J = 7.20$ Hz
3a	–	204.5	b **12**
	0.99	14.7	t, **e**, $^3J = 7.56$ Hz
	2.09	22.5	s, **a**
	2.22	20.3	m, **d**
	–	111.8	**c**
3b	–	190.8	**b**
	1.30	15.0	t, **g**
	2.14	22.2	s, **a**
	2.27	22.2	s, **e**
	3.80	63.7	q, **f**
	–	170.6	**d**
7	–	197.1	**b**
	1.03	15.3	t, **e**, $^3J = 7.42$ Hz
	1.99	25.3	s, **a**
	2.31	22.3	m, **d**
	–	114.2	**c**
	–	185.2	**b**
8	–	190.5	**b**
	0.89	13.6	t, **e**
	1.53	24.8	sept, **d**, $^3J = 7.38$ Hz
	2.13	24.3	s, **a**
	2.38	45.6	t, **c**, $^3J = 7.23$ Hz
9	–	209.3	**b**
	1.22	21.9	mult, **d**
	2.00	21.3	s, **a**
	4.98	67.6	quint, **c**, $^3J = 6.18$ Hz
6	–	170.5	**b**
Isopropoxy groups	1.18	25.4	mult
	1.23	26.6	mult
	4.00	64.2	s (br), m
	4.46	76.1	quint, m, $^3J = 5.85$ Hz
	4.73	77.1	sept, m, $^3J = 6.15$ Hz
	4.96	67.6	quint, m, $^3J = 6.18$ Hz

[a] The bold letters refer to the labels in the structural formulas in the left column.



Scheme 2

Conclusions

While the reaction of 1 or 2 molar equiv of unsubstituted acetylacetone with titanium, zirconium and aluminium alkoxides clearly gives acetyl acetonate substituted metal alkoxides, reaction of the 3-R-acac derivatives **1** and **3** was distinctly different in a two respects.

First, 6-(trimethoxysilyl)-2-hexanone (**5**) and isopropyl acetate (**6**) were identified in the reaction of **1** with 1–2 molar equiv of $Ti(O^iPr)_4$, in addition to the expected substitution product **2** [analogously for $Zr(OPr)_4$]. The compounds **5** and **6** clearly result from a cleavage of 3-R-acac-H. The reaction with 2 molar equiv of $Al(O^sBu)_3$ only results in the cleavage of **1** and only a minor proportion of a β-diketonate complex was observed. The cleavage reaction probably proceeds as indicated in Scheme 2. The dependence of the cleaved proportion of **1** on the kind of metal alkoxide ($Al \gg Ti \approx Zr$) may partially be due to the different Lewis acidity, but also to the higher covalency of the Al–O interaction and the shorter distance for the transfer of the OR group due to the smaller bonding radius of aluminium. The 3-alkyl substitution probably facilitates the cleavage reaction in a two-fold manner: by making the oxygen more nucleophilic and the alkoxide/β-diketonate substitution less facile. Therefore hydrodeacylation is not observed with unsubstituted acetylacetone under the same conditions.

In the case of $Ti(O^iPr)_4$ and $Zr(OPr)_4$, the coordinated proportion is larger than the cleaved proportion. This explains why the use of **1** nevertheless has a pronounced influence in getting homogeneous silica/titania mixed oxide gels.[8]

This is another example where a metal alkoxide reacts with a potentially coordinating organic compound both by formation of a metal complex and as a Lewis acidic catalyst in the transformation of the organic compound. The other example for such a dichotomy that we recently found was formation of a lysinate complex with $Zr(OR)_4$ *vs.* catalysis of lactame formation.[11]

The second difference is that with 2 molar equiv of 3-R-acac-H the reactions do not go to completion and small but significant amounts of unreacted 3-R-acac-H were spectroscopically observed in the reaction mixtures. The substitution of an alkoxide ligand of the alkoxide for a β-diketonate ligand is therefore less straightforward than in the case of unsubstituted acetylacetone. This is caused by the lower acidity of the proton in the 3-position due to the electron-donating alkyl group in this position. Incomplete substitution was previously observed in the reaction of 3-allyl-2,4-pentanedione with $Al(O^sBu)_3$, $Ti(OBu)_4$ and $Zr(OBu)_4$.[6] When a larger proportion of 3-R-acac-H is reacted, the equilibrium is shifted to the side of the β-diketonate complex and the Lewis acid-Lewis base interaction as in Scheme 2 is prevented. This explains why no cleavage is observed with a higher proportion of R-acac-H.

The results reported in this paper show that care must be taken when 3-substituted acetylacetone derivatives are used for the modification of metal alkoxides. The problems arising from incomplete reaction and dehydroacylation clearly originate from the presence of an alkyl substituent in the 3-position.

Experimental

General

All reactions were carried out using standard Schlenk techniques in a moisture- and oxygen-free argon atmosphere. Solvents were made water- and oxygen-free by standard methods.

NMR spectra were recorded on a Bruker Avance 300, 300.13 MHz {^1H}, 75.47 MHz {^{13}C} and 59.63 MHz {^{29}Si}, equipped with a 5 mm broadband probe head and a *z*-gradient unit. The solvents were $CDCl_3$ (99.8%, euriso-top) and CD_2Cl_2 (99.6%, euriso-top). 2D spectra were measured with Bruker standard pulse sequences: COSY (correlated spectroscopy), TOCSY (total correlation spectroscopy, mixing time was usually 160 ms), HSQC (heteronuclear single quantum correlation), $^1H/^{13}C$- and $^1H/^{29}Si$-HMBC (heteronuclear multiple bond correlation).

Syntheses and reactions

Synthesis of 3-acetyl-6-trimethoxysilylhexane-2-one (1). An amount of 15.0 g (0.1 mol) of NaI was dissolved in 60 ml of acetone. Chloropropyltrimethoxysilane (19.9 g, 0.1 mol) was added and the mixture was refluxed overnight. An amount of 13.8 g (0.1 mol) of K_2CO_3 and 10.0 g (0.1 mol) of acetylacetone was added and the mixture was again refluxed overnight. The reaction mixture was then filtered and the solvent removed *in vacuo*. The remaining liquid was distilled in vacuum (b.p. 90 °C/1 mbar). Yield: 12.1 g (46.1%). The by-product **4** could not be removed by distillation. IR (cm^{-1}): 2943 (m, C–H), 2943 (m, C–H), 2840 (m, Si–OCH_3), 1700 (m, C═O), 1585 (w, C–C and C–O), 1456 (w, C–H), 1358 (w, C–H), 1291 (w, CH_2), 1190 (m, Si–OCH_3), 1077 (s, Si–OCH_3), 995 (w), 955 (w), 896 (w), 807 (m), 758 (m, Si–C), 679 (w). ^{29}Si NMR ($^{29}Si^1H$ HMBC spectrum): −45.8 ppm. ^1H and ^{13}C NMR data: see Table 1.

Reaction of 3-acetyl-6-trimethoxysilylhexane-2-one (1) with $Ti(O^iPr)_4$. $Ti(O^iPr)_4$ was mixed with 2 molar equiv of **1** under argon and stirred for 15 min. A portion of 20 mg of the resulting mixture was diluted with 0.6 ml of $CDCl_3$ and used for the NMR experiments. The reaction of $Ti(O^iPr)_4$ with 1 molar equiv of **1** yielded the same products as in the reaction with 2 equiv. Because of the higher quality of the spectra of the reaction with 2 equiv of **1**, they were used for the structure assignments. IR (cm^{-1}): 2969 (m, C–H), 2840 (w, Si–OCH_3), 1701 (w, C═O), 1592 (m, C–C and C–O), 1460 (m, C–H), 1358 (m CH), 1290 (w, CH_2), 1122 (m, Ti–O^iPr), 1086 (s, Si–OCH_3), 1040 (s, O^iPr), 992 (m, CO of O^iPr), 884 (w, Ti–O^iPr), 848 (w), 808 (m). The NMR data are given in Table 2.

Reaction of 3-acetylpentane-2-one (3) with $Ti(O^iPr)_4$. The reactions with 1 or 2 molar equiv of **3** were performed as described for the reaction with **1**. The NMR data are given in Table 3.

Acknowledgements

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