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Friedel–Crafts acetylation and benzoylation of benzylsilanes and xanthenes

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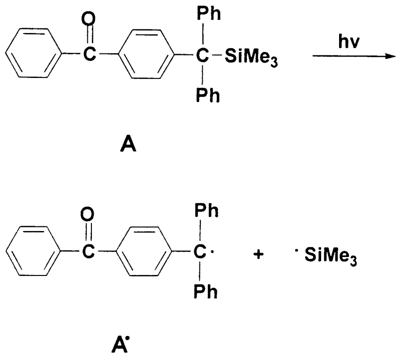
Abstract—The synthesis of *p*-acetyl and *p*-benzoyl derivatives of various benzylsilanes (p-$R^1CO–C_6H_4–CR^2R^3–SiMe_3$: R^1, R^2, R^3=Me, H, H; Me, H, Ph; Me, H, Me; Me, Me, Me; Ph, H, H; Ph, H, Ph; Ph, H, Me; Ph, Me, Me), xanthenes (3-benzoyl and 3,6-dibenzoyl), and 9-Me_3Si-xanthenes (3-benzoyl, 3,6-dibenzoyl, 3-acetyl and 3,6-diacetyl) using Friedel–Crafts reactions and typical Lewis acid catalysts ($AlCl_3$, $FeCl_3$, $ZnCl_2$) is described. Desilylation side reactions caused by $AlCl_3$ become significant in substrates with weak carbon–silicon bonds (e.g. $Ph_2CH–SiMe_3$), and in the case of $Ph_3C–SiMe_3$ only the desilylation product Ph_3CH was isolated. © 2002 Elsevier Science Ltd. All rights reserved.

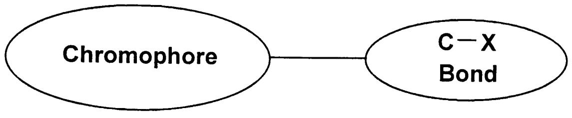
1. Introduction

In the era of printing and imaging technologies, photopolymerization reactions are of central importance, and there is a continuous interest in designing and preparing new and effective photoinitiator systems.[1–2] The photochemical properties of these systems and particularly their photodissociation ability is therefore crucial.

We studied recently the photodissociation of bichromophoric systems (Scheme 1) bearing the benzophenone-, acetophenone-, or the anilino-chromophore and a benzylic bond C–X (X=CMe_3, $SiMe_3$, NHPh), and found that a small decrease of the C–X bond strength increases considerable the photocleavage efficiency of the C–Si bond and the quantum yield of the corresponding radicals.[3–5] Particularly compound **A** proved to be a good photoinitiator system for methylmethacrylate and styrene polymerization,[6a] because of the very efficient formation of the $Me_3Si^{\cdot}$ radical[6b] which in fact triggers the polymerization process (Eq. (1)).[6a]



(1)



Scheme 1.

In the present paper, we describe the synthesis of a series of structurally similar *p*-acetyl and *p*-benzoyl derivatives of benzylsilanes and xanthenes (Schemes 2 and 3) using Friedel–Crafts reactions and typical Lewis acid catalysts ($AlCl_3$, $FeCl_3$, $ZnCl_2$). The aim was to prepare compounds analogous to **A**, containing a benzylic C–Si bond the strength of which would vary through consecutive methyl and/or phenyl substitution.

Although Friedel–Crafts reactions are widely used in organic synthesis for carbon–carbon bond formation,[7,8] and a variety of new and efficient catalysts have been developed,[9–12] little is known about acylation reactions on arylmethylsilanes.[13,14] However, it is reasonable to expect that the electron donating character of the CH_2SiMe_3 group ($\sigma_p=-0.21$)[15] will facilitate this electrophilic aromatic substitution reaction.

Keywords: Friedel–Crafts acylation; benzoylation; acetylation; benzylsilanes; xanthenes; desilylation.

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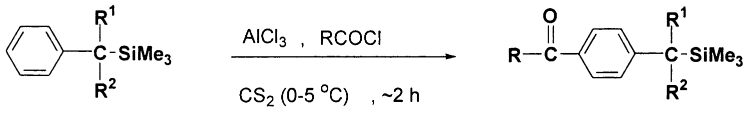
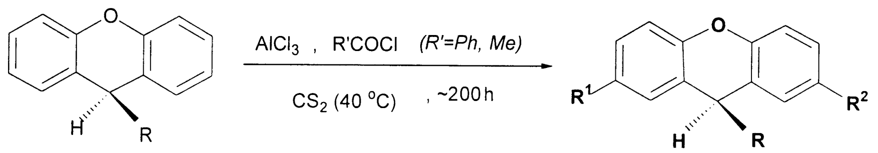


1 **2**

1 or 2	a	b	c	d	e	f	g	i
R	Ph	Ph	Ph	Ph	Me	Me	Me	Me
R^1	H	H	H	Me	H	H	H	Me
R^2	H	Ph	Me	Me	H	Ph	Me	Me

Scheme 2.



3 **4**

(**3a**, R=H,
(**3b**, R=SiMe$_3$)

4	a	b	c	d	e	f
R^1	PhCO	PhCO	PhCO	PhCO	MeCO	MeCO
R^2	H	PhCO	H	PhCO	H	MeCO
R	H	H	SiMe$_3$	SiMe$_3$	SiMe$_3$	SiMe$_3$

Scheme 3.

2. Results and discussion

2.1. Benzylsilane derivatives

The Friedel–Crafts acylation of the benzylsilanes **1a**–**i** with benzoyl chloride or acetyl chloride and AlCl$_3$ (Scheme 2) was carried out in the liquid phase at relatively low temperatures and with good yields.

The results are summarized in Table 1 and show that the yields of both the *p*-benzoylation (entries 1–4) and *p*-acetylation products (entries 5–8) decrease slightly down the series, as the C–Si bond becomes weaker due to increased methyl or phenyl substitution at the benzylic carbon atom. This tendency is maximized in the case of Ph$_3$C–SiMe$_3$ (entry 9), the compound possessing the weakest C–Si bond in the series;[16] here no any *p*-acylated product was obtained, but only the desilylation product Ph$_3$CH was isolated in ~100% yield.

$$\mathrm{Ph_3C\text{-}SiMe_3} \xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. } \mathrm{AlCl_3}} \mathrm{Ph_3C\text{-}H} \qquad (2)$$

Table 1. Friedel–Crafts benzoylation and acetylation of organosilicon compounds **1**

Entry	Organosilicon compound	Acylating reagent/catalyst	Reaction condition	Product	Yield (%)
1	**1a**	PhCOCl/AlCl$_3$	0–5°C, 2 h	**2a**	80
2	**1b**	PhCOCl/AlCl$_3$	0–5°C, 2 h	**2b**	66
3	**1c**	PhCOCl/AlCl$_3$	0–5°C, 2 h	**2c**	67
4	**1d**	PhCOCl/AlCl$_3$	0–5°C, 2 h	**2d**	45
5	**1e**	MeCOCl/AlCl$_3$	0–5°C, 2 h	**2e**	70
6	**1f**	MeCOCl/AlCl$_3$	0–5°C, 2 h	**2f**	70
7	**1g**	MeCOCl/AlCl$_3$	0–5°C, 2 h	**2 g**	63
8	**1i**	MeCOCl/AlCl$_3$	0–5°C, 2 h	**2i**	60
9	Ph$_3$C–SiMe$_3$	PhCOCl/AlCl$_3$	0–5°C, 2 h	Ph$_3$CH	100
10	Ph$_3$C–SiMe$_3$	AlCl$_3$	0–5°C, 2 h	Ph$_3$CH	100
11	**1b**	AlCl$_3$	0–5°C, 2 h	Ph$_2$CH+**1b**	60+40
12	**1a**	AlCl$_3$	0–5°C, 2 h	**1a**	100

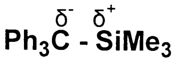
Table 2. The influence of catalyst and solvent on the yield of **2b**

Entry	$Ph_2CH-SiMe_3$ (mmol)	PhCOCl (mmol)	Catalyst (mmol)	Solvent (10 ml)	Yield (%)
1	16.6	34.2	$AlCl_3$ (16.7)	CS_2 (20 ml)	66
2	15.3	7.9	$AlCl_3$ (7.5)	CS_2	40
3	15.3	7.9	$FeCl_3$ (7.5)	CS_2	35
4	15.3	7.9	$ZnCl_2$ (7.5)	CS_2	25
5	15.0	7.9	$AlCl_3$ (7.5)	Nitrobenzene	42
6	15.0	7.9	$AlCl_3$ (7.5)	CH_2Cl_2	35
7	15.0	7.9	$AlCl_3$ (traces)	CS_2	15
8	15.0	7.9	$AlCl_3$ (15)	CS_2	22

Table 3. Friedel–Crafts benzoylation and acetylation of xanthene (**3a**) and 9-(trimethylsilyl)xanthene (**3b**)

Entry	Organosilicon compound	Acylating reagent/catalyst	Reaction condition	Product	Yield (%)
1	**3a**	$PhCOCl/AlCl_3$	~40°C, 2 h	**4a**	93
2	**3a**	$PhCOCl/AlCl_3$	~40°C, 20 h	**4b**	63
3	**3b**	$PhCOCl/AlCl_3$	~40°C, 2 h	**4c**	56
4	**3b**	$PhCOCl/AlCl_3$	~40°C, 20 h	**4d**	64
5	**3b**	$MeCOCl/AlCl_3$	~40°C, 2 h	**4e**	65
6	**3b**	$MeCOCl/AlCl_3$	~40°C, 20 h	**4f**	60

This observation prompted us to examine the effect of the catalyst $AlCl_3$ itself on $Ph_3C-SiMe_3$, i.e. without the acylating reagent (PhCOCl); following exactly the same procedure as before, we found Ph_3CH as the only product isolated (Eq. (2), Table 1, entry 10). In the case of $Ph_2CH-SiMe_3$ as a substrate, a mixture of diphenylmethane Ph_2CH_2 and the starting material ($Ph_2CH-SiMe_3$) was obtained under the same conditions (Table 1, entry 11), while $PhCH_2-SiMe_3$ (possessing the strongest C–Si bond in the series) remains totally unaffected by the action of $AlCl_3$ under the same conditions (Table 1, entry 12).



$$Ph_3\overset{\delta^-}{C} - \overset{\delta^+}{Si}Me_3 \qquad (3)$$

Obviously, the Lewis acid attacks, due to its electrophilic character, the benzylic C–Si bond of $Ph_3C-SiMe_3$ (and to a lesser extent that of $Ph_2CH-SiMe_3$), but not the C–Si bond of $PhCH_2-SiMe_3$, because the former is much weaker and better polarized; this polarization is expected to increase by increasing phenylation at the benzylic carbon atom (better stabilization of the negative charge, Eq. (3)). In addition, the steric hindrance of the bulky trityl group probably increases the weakness of the bond. All the above facts are reflected in the observed product yields.

Generally, the cleavage of the C–Si bond upon electrophilic attack is a well-known process in arylsilanes (*ipso*-silyl cleavage) and vinylsilanes, both undergoing desilylation.[17,18]

In order to suppress the C–Si bond cleavage of diphenylmethyltrimethylsilane (**1b**) and improve possibly the yield of the *p*-acylated product, a less acidic catalyst $FeCl_3$ or $ZnCl_2$[19,20] was used (Table 2). It was found that these Lewis acid catalysts did not improve the yield of the acylation reaction (entries 3 and 4); in fact the lower yields observed are attributed to a lower reactivity of the catalysts since no desilylation products were obtained. Also the yield is not markedly affected by changing other factors such as the solvent (entries 2, 5 and 6) or the molar ratios of the catalyst to substrate (entries 2, 7 and 8).

2.2. Xanthene derivatives

The acylation reaction of the xanthene derivatives (Scheme 2) was carried out in the same manner. However, this reaction requires much more time and higher temperatures (~20 h and 40°C), particularly for the preparation of disubstituted products (Table 3).

The yields were relatively high, and in contrast to $Ph_2CH-SiMe_3$ the C–Si bond remains intact after treatment with $AlCl_3$. Presumably, in the present case the electron donating ability of the oxygen reduces the polarization of C–Si bond and simultaneously directs the electrophilic aromatic substitution at the 2- and 7-position (*para*- to the oxygen bridge and *meta*- to CH_2SiMe_3) and not to positions 3 and 6 which are *para*- to CH_2SiMe_3. It is known that the OH group is a much stronger activating group ($\sigma_p=-0.37$)[15] than the CH_2SiMe_3 ($\sigma_p=-0.21$),[15] and obviously controls the regiospecificity of the substitution.

3. Experimental

The preparations were carried out under argon atmosphere using Schlenk techniques. Melting points were taken on a Büchi 510 apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer FT-IR SpectrumGX or a Perkin–Elmer 783B spectrometer as KBr pellets or neat liquid. Elemental analyses were performed on a Perkin–Elmer 2400CHN or a Carlo Erba 1106 elemental analyzer and for the liquid samples on a LECO, CHNS-932 analyzer. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ solutions on a Brucker (AMX-400, AM-300, or AC-250) spectrometer. Chemical shifts (δ) are given in ppm and referenced with respect to the residual signals of the solvent, *J* values in

Hz. Mass spectra were obtained on a Finnigan MAT 8400 (high resolution) instrument using EI. For the GC–MS analyses a HP 5890 gas chromatograph equipped with a 5971A mass selective detector or a Shimadzu QP-5000 instrument were used. Analytical TLC was carried out on Fluka silica gel 60 F_{254}. Preparative flash chromatography was carried out using Merck 9385 silica gel. THF and ether were dried by distillation over Na/benzophenone ketyl and stored under Ar, while $AlCl_3$ was sublimed prior to use.

3.1. Preparation of benzylsilane derivatives

Benzylsilane (**1a**) and xanthene was purchased from Aldrich, diphenylmethyl(trimethylsilyl)methane (**1b**) and triphenylmethyl(trimethylsilyl)methane (**5**) have been described in the literature.[21,22] (1-Phenylethyl) trimethylsilane (**1c**) and phenylisopropyl trimethylsilane (**1d**) were prepared according to general methods reported by Coughlin et al.[23]

3.1.1. (1-Phenylethyl)trimethylsilane (1c).[23b] This compound was prepared from α-phenylethyl bromide (10.15 ml, 0.08 mol), Me_3SiCl (8.7 g, 0.08 mol) and Mg (1.92 g, 0.08 mol) in 110 ml abs. THF under argon atmosphere. 10.13 g (71%) of **1c** was obtained as a colorless liquid (bp 88–90°C/15 Torr, lit. 98–100°C/15 Torr[23b]); ν_{max} (neat) 3082, 3061, 3024, 2957, 2871, 1602, 1495, 1450, 1248, 836 (C–Si), 771, 749, 699 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.06–7.28 (5H, m, Ar-H), 2.22 (1H, q, J=7.6 Hz, C*H*), 1.39 (3H, d, J=7.6 Hz, C*H*$_3$), −0.02 (9H, s, Si*Me*$_3$); δ_C (62.9 MHz, $CDCl_3$) 145.9, 127.9, 126.0, 124.2 (C_{arom}), 29.7 (*C*H–$SiMe_3$), 14.9 (*C*H_3), −4.3 (Si*Me*$_3$); GC–MS *m*/*z* (%): 178 (M^+, 25), 135 (46), 121 (12), 105 (M^+-SiMe_3, 21), 77 (18), 73 ($SiMe_3$, 100).

3.1.2. 2-Phenyl-2-(trimethylsilyl)propane (1d).[23c] This compound was prepared from 2-phenylisopropyl chloride (14.6 g, 0.09 mol), Me_3SiCl (7.6 g, 0.07 mol) and Mg (1.68 g, 0.07 mol) in 70 ml abs. THF under argon atmosphere. 9.16 (68%) of **1d** was isolated as a colorless liquid (bp 85–87°C/15 Torr, lit. 220–221°C[23c]); ν_{max} (neat) 3087, 3057, 3033, 2961, 2865, 1600, 1494, 1248, 837 (C–Si), 777, 756, 698 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.08–7.41 (5H, m, Ar-H), 1.41 (6H, s, C*H*$_3$), −0.04 (9H, s, $SiMe_3$); δ_C (62.9 MHz, $CDCl_3$) 148.9, 127.7, 126.1, 124.0 (C_{arom}), 26.9 (*C*–$SiMe_3$), 23.8 (*C*H_3), −4.1 (Si*Me*$_3$); GC–MS *m*/*z* (%): 192 (M^+, 48), 135 (39), 121 (12), 118 (PhC(Me)═CH_2, 70), 103 (17), 91 (77), 73 ($SiMe_3$, 100).

3.1.3. 9-(Trimethylsilyl)xanthene (3b). This compound was prepared from 10.0 g (55 mmol) xanthene in 70 ml abs. ether, 70 ml (55 mmol, 0.78 M solution in abs. ether) *n*-BuLi and 7 ml (56 mmol) of Me_3SiCl using the method already described for Ph_2CH–$SiMe_3$:[21c] 11.3 g (81%) of **3b** was obtained as white crystals, mp 117–119°C (ethanol), (lit. 119–120°C);[24] [Found: C, 75.70; H, 7.17. $C_{18}H_{18}OSi$ requires C, 75.54; H, 7.13%]; ν_{max} (KBr) 3050, 3020, 2942, 2880, 2860, 1586, 1516, 1467, 1443, 1441, 836 (C–Si) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.95–7.11 (8H, m, Ar-H), 3.49 (1H, s, C*H*), 0.04 (9H, s, Si*Me*$_3$); δ_C (62.9 MHz, $CDCl_3$) 151.7, 127.5, 126.1, 125.4, 123.0, 116.1 (C_{arom}), 34.7 (*C*H–$SiMe_3$), −3.4 (Si*Me*$_3$).

3.2. Acylation of benzylsilane derivatives 1a–i (Scheme 1)

General procedure. An excess of fresh distilled benzoyl chloride or acetyl chloride (34.2 mmol) was added to a solution of the silyl compound (16.6 mmol) in absolute CS_2 (20 ml) under argon. The mixture was cooled (0–5°C) and then well-powdered $AlCl_3$ (16.7 mmol) was added in small portions while stirred vigorously. During the reaction the temperature was kept between 0 and 5°C. The reaction progress was monitored by TLC (SiO_2, Hexane/EtOAc 9/1). The resulting mixture was added to ether/ice water and the organic layer was separated and washed with water, sat. $NaHCO_3$ and again water and dried over $MgSO_4$. After solvent evaporation the acylated product was separated by column chromatography.

3.2.1. 4-(Trimethylsilylmethyl)benzophenone (2a). According to the general method **2a** was isolated as white crystals (3.3 g, 80%), mp 66–67°C (ethanol);[13,14] ν_{max} (KBr) 3060, 3040, 2952, 2895, 1645 (C═O), 1597, 1275, 1243, 856 (C–Si) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.77 (2H, dd, J=8.3, 1.5 Hz, Ar-H), 7.42–7.58 (3H, m, Ar-H), 7.69 (2H, d, J=8.3 Hz, Ar-H), 7.07 (2H, d, J=8.3 Hz, Ar-H), 2.18 (2H, s, C*H*$_2$), 0.00 (9H, s, Si*Me*$_3$); δ_C (62.9 MHz, $CDCl_3$) 196.4 (*C*═O), 146.7, 138.2, 133.4, 131.9, 130.3, 129.8, 128.1, 127.7 (C_{arom}), 27.9 (*C*H_2–$SiMe_3$), −1.9 (Si*Me*$_3$); GC–MS *m*/*z* (%): 268 (M^+, 28), 253 (3), 105 (PhCO, 10), 77 (12), 73 ($SiMe_3$, 100).

3.2.2. 4-[Phenyl(trimethylsilyl)methyl]benzophenone (2b). According to the general method **2b** was obtained as white crystals (3.8 g, 66%), mp 114–115°C (ethanol) after purification using column chromatography (silica gel 60, petroleum ether/ethylacetate 9/1); [Found: C, 79.89; H, 7.00. $C_{23}H_{24}OSi$ requires C, 80.18; H, 7.02%]; ν_{max} (KBr) 3078, 3059, 3028, 2952, 2897, 1650 (C═O), 1598, 1282, 1248, 835 (C–Si), 753, 703 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.24–7.78 (14H, m, Ar-H), 3.62 (1H, s, C*H*), 0.05 (9H, s, Si*Me*$_3$); δ_C (62.9 MHz, $CDCl_3$) 196.4 (*C*═O), 148.5 (q), 141.9 (q), 138.0 (q), 134.3 (q), 132.1, 130.4, 129.9, 129.0, 128.5, 128.2, 125.5 [C_{arom}], 46.7 (*C*H–$SiMe_3$), 1.7 (Si*Me*$_3$).

3.2.3. 4-[Methyl(trimethylsilyl)methyl]benzophenone (2c). According to the general method 3.0 g (67%) of **2c** was obtained as colorless liquid after purification using column chromatography (silica gel 60, petroleum ether/ethylacetate 10/1); [Found: C, 76.32; H, 7.86. $C_{18}H_{22}OSi$ requires C, 76.54; H, 7.85%]; ν_{max} (neat) 3061, 3028, 2957, 2872, 1656 (C═O), 1602, 1281, 1249, 857, 838 (C–Si) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.12–7.79 (9H, m, Ar-H), 2.28 (1H, q, J=7.4 Hz, C*H*), 1.39 (3H, d, J=7.4 Hz, C*H*$_3$), −0.04 (9H, s, Si*Me*$_3$); δ_C (100 MHz, $CDCl_3$) 196.4 (*C*═O), 152.0 (q), 138.2 (q), 133.6 (q), 132.7, 130.2, 129.8, 128.1, 126.7 [C_{arom}], 30.6 (*C*–$SiMe_3$), 14.5 (*C*H_3), −3.4 (Si*Me*$_3$); GC–MS *m*/*z* (%): 282 (M^+, 27), 267 (M^+-Me, 3), 105 (PhCO, 12), 77 (Ph, 22), 73 ($SiMe_3$, 100); HRMS (EI): M^+, found 282.1432. $C_{18}H_{22}OSi$ requires 282.1439.

3.2.4. 4-[Dimethyl(trimethylsilyl)methyl]benzophenone (2d). According to the general method **2d** was obtained as white crystals (2.2 g, 45%), mp 80–82°C (ethanol); [Found: C, 77.06; H, 8.21. $C_{19}H_{24}OSi$ requires C, 77.03; H, 8.17%];

ν_{max} (KBr) 3081, 3032, 2958, 2870, 1652 (C═O), 1600, 1281, 1252, 847 (C–Si) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.28–7.80 (9H, m, Ar-H), 1.41 (6H, s, CH_3), −0.07 (9H, s, Si*Me*$_3$); δ_C (100 MHz, $CDCl_3$) 196.4 (*C*═O), 154.9, 138.2, 131.9, 129.9, 129.8, 128.1, 125.9, 125.8 (C_{arom}), 28.3 (*C*–$SiMe_3$), 23.8 (CH_3), −4.2 (Si*Me*$_3$); GC–MS *m/z* (%): 296 (M^+, 27), 281 (M^+−Me, 20), 105 (PhCO, 12), 77 (Ph, 18), 73 ($SiMe_3$, 100).

3.2.5. 4-(Trimethylsilylmethyl)acetophenone (2e). According to the general procedure 2.38 g (70%) of **2e** was isolated after fractional distillation (75°C/0.03 Torr). The product solidified after a while, mp 44–45°C (ethanol), [lit. 39–40.5°C];[13] ν_{max} (KBr) 3028, 2958, 2895, 1676 (C═O), 1602, 1270, 1248, 853 (C–Si) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.81–7.83 (2H, d, *J*=8.2 Hz, Ar-H), 7.05–7.07 (2H, d, *J*=8.1 Hz, Ar-H), 2.56 (3H, s, CH_3), 2.17 (2H, s, CH_2), −0.07 (9H, s, Si*Me*$_3$); δ_C (62.9 MHz, $CDCl_3$) 197.7 (*C*═O), 147.2, 133.4, 128.4, 127.9 (C_{arom}), 27.9 (CH_2–$SiMe_3$), 26.3 (CH_3CO), −2.0 (Si*Me*$_3$); GC–MS *m/z* (%): 206 (M^+, 35), 191 (M^+−Me, 9), 115 (3), 73 ($SiMe_3$, 100).

3.2.6. 4-[Phenyl(trimethylsilyl)methyl]acetophenone (2f). According to the general method this product was obtained as white crystals (3.3 g, 70%), mp 66–67°C (ethanol) after column chromatography (SiO_2, hexane/ethylacetate 9/1); [Found: C, 76.63; H, 7.89. $C_{18}H_{22}OSi$ requires C, 76.54; H, 7.85%]; ν_{max} (KBr) 3050, 3020, 2945, 2885, 2865, 1670 (C═O), 1598, 1273, 1249, 845 (C–Si), 750, 703 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.82 (2H, d, *J*=8.3 Hz, Ar-H), 7.10–7.31 (7H, m, Ar-H), 3.59 (1H, s, C*H*), 2.54 (3H, s, CH_3), 0.03 (9H, s, Si*Me*$_3$); δ_C (62.9 MHz, $CDCl_3$) 197.7 (*C*═O), 149.1, 141.8, 134.2, 128.9, 128.5, 125.5 (C_{arom}), 48.7 (*C*H–$SiMe_3$), 26.4 (CH_3CO), −1.8 (Si*Me*$_3$).

3.2.7. 4-[Methyl(trimethylsilyl)methyl]acetophenone (2g). 2.3 g (63%) of **2g** was prepared according to the general procedure. The white crystals melt around the room temperature (ethanol); [Found: C, 70.88; H, 9.27. $C_{13}H_{20}OSi$ requires C, 70.85; H, 9.15%]; ν_{max} (neat) 3031, 3001, 2957, 2900, 2873, 1682 (C═O), 1603, 1270, 1249, 850 (C–Si) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.86 (2H, d, *J*=8.2 Hz, Ar-H), 7.11 (2H, d, *J*=8.2 Hz, Ar-H), 2.56 (3H, s, CH_3CO), 2.28 (1H, q, *J*=7.4 Hz, C*H*), 1.38 (3H, d, *J*=7.4 Hz, CH_3), −0.05 (9H, s, $SiMe_3$); δ_C (100 MHz, $CDCl_3$) 197.8 (*C*═O), 152.5, 133.7, 128.2, 126.9 (C_{arom}), 30.7 (*C*H–$SiMe_3$), 26.3 (CH_3CO), 14.4 (CH_3), −3.4 (Si*Me*$_3$); GC–MS *m/z* (%): 220 (M^+, 23), 177 (M^+−MeCO, 3), 73 ($SiMe_3$, 100); HRMS (EI): M^+, found 220.1281. $C_{13}H_{20}OSi$ requires 220.1283.

3.2.8. 4-[Dimethyl(trimethylsilyl)methyl]acetophenone (2i). 2.33 g (60%) of **2i** was isolated according to the general procedure, mp 44–46°C (ethanol) after purification with column chromatography (silica gel 60, petroleum ether/ethylacetate 10/1); [Found: C, 71.73; H, 9.50. $C_{14}H_{22}OSi$ requires C, 71.74; H, 9.47%]; ν_{max} (KBr) 3061, 3044, 2960, 2869, 1681 (C═O), 1602, 1273, 1247, 838 (C–Si) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.87 (2H, d, *J*=8.2 Hz, Ar-H), 7.26 (2H, d, *J*=8.2 Hz, Ar-H), 2.56 (3H, s, CH_3CO), 1.38 (6H, s, CH_3), −0.08 (9H, s, Si*Me*$_3$); δ_C (100 MHz, $CDCl_3$) 197.7 (*C*═O), 155.4, 133.2, 127.8, 126.1 (C_{arom}), 28.3 (*C*–$SiMe_3$), 26.3 (CH_3CO), 23.7 (CH_3), −4.3 (Si*Me*$_3$); GC–MS *m/z* (%): 234 (M^+, 17), 219 (M^+−Me, 2), 177 (M^+−MeCO, 3), 73 ($SiMe_3$, 100).

3.3. Xanthene derivatives

*General procedure (monosubstituted derivatives **4a**, **b** and **e**).* In a mixture of xanthene (11 mmol) and $AlCl_3$ (13 mmol) in carbon disulfide (20 ml) or in a mixture of 9-(trimethylsilyl)xanthene (7.86 mmol) and $AlCl_3$ (8.6 mmol) in carbon disulfide (10 ml) was added 13 or 8.6 mmol benzoyl (or acetyl) chloride, respectively, during a period of ~15 min. The mixture was heated at ~40°C until the reaction was completed (TLC control). The mixture was hydrolyzed with water/ice mixture (20 ml) and diluted with dichloromethane (30 ml). The organic layer was neutralized with a 10% solution of $NaHCO_3$ and was dried over $NaSO_4$. Removal of the solvent under vacuum gave the crude product, which was purified by recrystallization.

Disubstituted derivatives **4c**, **d** and **f**. For the synthesis of disubstituted derivatives the molar ratio between the xanthene substrate, the $AlCl_3$ catalyst and the benzoyl (or acetyl) chloride was 1:2:2, respectively.

3.3.1. 2-(Benzoyl)xanthene (4a). 2.9 g (93%) of **4a** was obtained as white crystals according to the general method, mp 149–150°C, (ethanol/chloroform 3/2); [Found: C, 84.20; H, 4.88. $C_{20}H_{14}O_2$ requires C, 83.90; H, 4.93%]; ν_{max} (KBr) 3040, 2913, 2835, 1642 (C═O), 1594, 1478, 1449, 1246, 752, 728, 693 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.78 (2H, d, *J*=7.5 Hz, Ar-H), 7.71 (1H, s, xanthene-H_1), 7.67 (1H, dd, *J*=8.4, 2.1 Hz, xanthene-H_3), 7.57 (1H, tt, *J*=7.4, 1.5 Hz, Ar-H), 7.47 (2H, tt, *J*=7.5, 1.5 Hz, Ar-H), 7.01–7.24 (5H, m, xanthene-H_{4-8}), 4.09 (2H, s, xanthene-H_9); δ_C (62.9 MHz, $CDCl_3$) 195.5 (*C*═O), 155.4 (q), 151.3 (q), 138.0 (q), 132.3 (q), 132.1, 131.7, 130.5, 129.8, 129.0, 128.2, 127.9, 123.7, 120.5 (q), 119.9 (q), 116.6, 116.3 [C_{arom}], 27.6 (CH_2); MS (EI, 70 eV): *m/z* (%): 286 (M^+, 100), 209 (M^+−C_6H_5, 38), 181 (M^+−COC_6H_5, 54), 105 (C_6H_5CO, 14), 77 (C_6H_5, 25).

3.3.2. 2,7-(Dibenzoyl)xanthene (4b). According to the general method **4b** was obtained as white crystals 2.7 g (63%), mp 253–254°C, (toluene); [Found: C, 82.87; H, 4.52. $C_{27}H_{18}O_3$ requires C, 83.06; H, 4.65%]; ν_{max} (KBr) 3042, 2910, 2835, 1642 (C═O), 1615, 1590, 1478, 1437, 1275, 727, 690 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.78 (4H, dd, *J*=7.6, 1.4 Hz, Ar-H), 7.73 (2H, s, xanthene-$H_{1,8}$), 7.71 (2H, dd, *J*=8.4, 2.1 Hz, xanthene-$H_{3,6}$), 7.59 (2H, tt, *J*=7.4, 1.3 Hz, Ar-H), 7.49 (4H, tt, *J*=7.6, 1.3 Hz, Ar-H), 7.15 (2H, d, *J*=8.3 Hz, xanthene-$H_{4,5}$), 4.16 (2H, s, xanthene-H_9); δ_C (62.9 MHz, $CDCl_3$) 195.4 (*C*═O), 154.6, 137.8, 133.1, 132.3, 131.6, 130.7, 129.8, 128.3, 120.0, 116.5 (C_{arom}), 27.5 (CH_2); MS (EI, 70 eV): *m/z* (%): 390 (M^+, 100), 313 (M−C_6H_5, 45), 285 (M^+−COC_6H_5, 50), 105 (C_6H_5CO, 32), 77 (C_6H_5, 34).

3.3.3. 2-Benzoyl-9-(trimethylsilyl)xanthene (4c). 1.58 g (56%) of **4c** was isolated as white crystals mp 112–113°C (ethanol/chloroform 1/1); [Found: C, 77.13; H, 5.83; Si, 8.41. $C_{23}H_{22}O_2Si$ requires C, 77.06; H, 6.19; Si, 7.83%];

ν_{max} (KBr) 3061, 2960, 2895, 1650 (C=O), 1598, 1257, 1245, 840 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.77 (2H, d, *J*=7.4 Hz, Ar-H), 7.61 (1H, dd, *J*=8.4, 1.8 Hz, xanthene-H_3), 7.55 (1H, t, *J*=7.3 Hz, Ar-H), 7.47 (2H, t, *J*=7.5 Hz, Ar-H), 7.47 (1H, s, xanthene-H_1), 7.12 (1H, t, *J*=7.6 Hz, xanthene-H_6), 7.06 (1H, d, *J*=8.4 Hz, xanthene-H_4), 7.01–7.04 (2H, m, xanthene-$H_{7,8}$), 6.85 (1H, d, *J*=7.6 Hz, xanthene-H_5), 3.43 (1H, s, xanthene-H_9), −0.03 (9H, s, SiCH_3); δ_C (100 MHz, $CDCl_3$) 195.5 (*C*=O), 155.4 (q), 151.1 (q), 138.1 (q), 132.5 (q), 131.9, 129.8, 129.6, 129.1, 128.1, 127.5, 126.4, 125.5 (q), 124.6 (q), 123.6, 116.2, 115.9 [C_{arom}], 34.6 (*C*–$SiMe_3$), −3.4 (SiMe_3); GC–MS *m*/*z* (%): 358 (M^+, 46), 285 (M^+-SiMe_3, 41), 180 (xanthene, 21), 105 (PhCO, 3), 77 (Ph, 18), 73 ($SiMe_3$, 100).

3.3.4. 2,7-Dibenzoyl-9-(trimethylsilyl)xanthene (4d). 2.31 g (64%) of **4d** was obtained as pale yellow crystals, mp 199–200°C, (ethanol/chloroform 1/1); [Found: C, 78.10; H, 5.47. $C_{30}H_{26}O_2Si$ requires C, 77.89; H, 5.66; Si, 6.07%]; ν_{max} (KBr) 3042, 3014, 2948, 1648 (C=O), 1596, 1272, 1248, 842 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.77 (4H, d, *J*=7.5 Hz, Ar-H), 7.63 (2H, dd, *J*=8.4, 1.7 Hz, xanthene-$H_{3,6}$), 7.59 (2H, t, *J*=7.2 Hz, Ar-H), 7.46 (4H, t, *J*=7.5 Hz, Ar-H), 7.46 (2H, s, xanthene-$H_{1,8}$), 7.11 (2H, d, *J*=8.4 Hz, xanthene-$H_{4,5}$), 3.48 (1H, s, xanthene-H_9), 0.00 (9H, s, SiCH_3); δ_C (62.9 MHz, $CDCl_3$) 195.5 (*C*=O), 154.6 (q), 137.9 (q), 133.2, 132.2 (q), 129.8, 129.8, 129.4, 128.2, 125.0 (q), 116.2 [C_{arom}], 34.6 (*C*–$SiMe_3$), −3.5 (SiMe_3); GC–MS *m*/*z* (%): 358 (M^+, 46), 285 (M^+-SiMe_3, 41), 180 (xanthene, 21), 105 (PhCO, 3), 77 (Ph, 18), 73 ($SiMe_3$, 100).

3.3.5. 2-Acetyl-9-(trimethylsilyl)xanthene (4e). According to the general method **4e** was obtained as white crystals: 1.52 g (65%), mp 124–125°C (CCl_4); [Found: C, 72.87; H, 6.73. $C_{18}H_{20}O_2Si$ requires C, 72.92; H, 6.80; Si, 6.07%]; ν_{max} (KBr) 2966, 2840, 1677 (C=O), 1617, 1248, 1268, 845, 827 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.76 (dd, 1H, *J*=8.4, 2.0 Hz, xanthene-H_3), 7.64 (1H, d, *J*=1.9 Hz, xanthene-H_1), 7.0–7.15 (5H, m, xanthene-H_{4-8}), 3.47 (1H, s, xanthene-H_9), 2.60 (3H, s, CH_3), 0.06 (9H, s, SiCH_3); δ_C (75 MHz, $CDCl_3$) 196.7 (*C*=O), 155.8 (q), 151.1 (q), 132.5 (q), 128.0, 127.5, 127.3, 126.4, 125.6 (q), 124.6 (q), 123.7, 116.9, 116.2 [C_{arom}], 34.6 (*C*–$SiMe_3$), 26.4 (CH_3), −3.5 (SiMe_3); GC–MS *m*/*z* (%): 296 (M^+, 100), 223 (M^+-SiMe_3, 45), 73 ($SiMe_3$).

3.3.6. 2,7-Diacetyl-9-(trimethylsilyl)xanthene (4f). According to the general method 1.6 g (60%) of **4f** was isolated as white crystals after column chromatography (silica gel 60, petroleum ether/ethylacetate 2:1) and recrystallization from an ethanol/chloroform mixture (1:1), mp 186–188°C; [Found: C, 71.41; H, 6.45. $C_{20}H_{22}O_3Si$ requires C, 70.99; H, 6.55%]; ν_{max} (KBr) 2970, 2890, 1682 (C=O), 1615, 1254, 841, 827 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.78 (2H, dd, *J*=8.5, 2.1 Hz, xanthene-$H_{4,5}$), 7.64 (2H, d, *J*=2.1 Hz, xanthene-$H_{1,8}$), 7.08 (2H, d, *J*=8.5 Hz, xanthene-$H_{3,6}$), 3.53 (1H, s, xanthene-H_9), 2.60 (6H, s, CH_3), 0.01 (9H, s, SiCH_3); δ_C (62.9 MHz, $CDCl_3$), 196.7 (*C*=O), 154.8 (q), 133.0 (q), 128.0, 127.6, 124.9 (q), 116.3 [C_{arom}], 34.4 (*C*–$SiMe_3$), 26.4 (CH_3), −3.6 (SiMe_3); GC–MS *m*/*z* (%): 338 (M^+, 26), 265 (M^+-SiMe_3, 14), 222 (14), 179 (xanthene, 11), 73 ($SiMe_3$, 100).

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