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Hydrosilylation of carbonyl compounds catalysed by alkali metal fluorides in the presence of crown ethers

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Abstract

Hydrosilylation of the C=O bond with dimethylphenylsilane proceeds readily in low-polarity solvents (dichloromethane, benzene, THF) in the presence of the catalytic pair MF/18-crown-6 (M = Cs, Rb, K), with caesium and rubidium fluorides being the most active. Using the CsF/18-crown-6 pair, the hydrosilylation of a number of aromatic and heteroaromatic aldehydes and ketones has been carried out. Silyl ethers of the corresponding alcohols have been prepared in good yields.

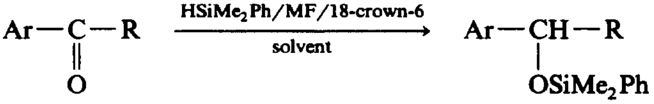
Introduction

Catalytic hydrosilylation of aldehydes and ketones is one method for their reduction to the corresponding alcohols. Usually transition metal complexes are used as catalysts of these reactions [1–6]. Fluoride ion-induced addition of hydrosilanes to C=O bond, though known since 1973 [7,8] has been less thoroughly studied. The reaction has been carried out under heterogeneous conditions without solvent [9–11] or in aprotic polar solvents (MeCN, DMSO, DMFA) [12,13]; alkali metal fluorides (usually KF or CsF) in, at least, stoichiometric concentration were used as a source of F^-. Under homogeneous conditions the reaction is effectively catalysed by tetrabutylammonium fluoride in DMSO [14] or in HMPTA [15,16], as well as by tris(diethylamino)sulphonium difluorotrimethylsilicate in HMPTA [16]. It has been shown that potassium and caesium fluorides (in catalytic concentrations) in HMPTA are less effective than $Bu_4N^+F^-$, at the same time the latter has low activity in dichloromethane and tetrahydrofuran [16]. The homogeneous catalytic reduction of the C=O bond using hydrosilanes [15,16] is preferable to the stoichiometric method, however high yields of hydrosilylation products were obtained only in the case of aldehydes; moreover, the preparation of anhydrous $Bu_4N^+F^-$ is a laborious and time-consuming procedure.

Recently, we have found that the hydrosilylation of carbonyl compounds can be carried out successfully in low-polarity dichloromethane in the presence of catalytic amounts of CsF as the source of F^- and 18-crown-6 as the phase-transfer agent [17]. The aim of the present work is to clarify the influences of solvent, alkali metal fluoride, crown ether and the carbonyl compound on the process to determine the scope and limitations of this method.

Results and discussion

We have studied the reactions of aromatic and heterocyclic aldehydes and ketones (**1**) with dimethylphenylsilane in low-polarity solvents using CsF, RbF, KF, NaF and LiF and the source of fluoride ion. 18-Crown-6, 15-crown-5 and 12-crown-4 were used as phase-transfer agents. The reactions were carried out at room temperature, the course of the processes was monitored by GLC and GLC-MS analysis. The influence of alkali metal fluoride, solvent and phase-transfer agent on the hydrosilylation rate was studied specifically in the case of the reaction of acetophenone with $HSiMe_2Ph$ (on semi-micro scale) (Table 1).



$$\mathrm{Ar{-}C({=}O){-}R} \xrightarrow[\text{solvent}]{\mathrm{HSiMe_2Ph/MF/18\text{-}crown\text{-}6}} \mathrm{Ar{-}CH(OSiMe_2Ph){-}R}$$

(1a–j) **(2a–j)**

CsF/18-crown-6 and RbF/18-crown-6 were found to be the most effective catalytic pairs. In their presence the silyl ether **2** (Ar = Ph, R = Me) can be obtained in quantitative yield (measured by GLC). None of the solvents studied had a strong influence; in most cases from the point of view of the reaction rate the use of dichloromethane is preferable. Potassium fluoride in the presence of 18-crown-6 is considerably less active than caesium and rubidium fluorides although the K^+ ion (ionic diameter 2.66 Å) and crown ether (diameter of cavity 2.6–3.2 Å) [18] do show best fit. Rb^+ and Cs^+ ions (ionic diameter 2.96 and 3.34 Å, respectively [18]) are, at first sight, less suitable for complexation with 18-crown-6, however these metal fluorides are extremely active catalysts for acetophenone hydrosilylation. High

Table 1

Fluoride ion-induced hydrosilylation of acetophenone with dimethylphenylsilane (25 °C, the molar ratio $PhCOMe:HSiMe_2Ph:F^-$:crown ether = 1:1.1:0.1:0.05)

Catalyst	Solvent	Yield of $PhCH(OSiMe_2Ph)Me$ (%) [a]	Reaction time (h)
CsF/18-crown-6	CH_2Cl_2	100	5
CsF	CH_2Cl_2	<1	24
CsF/18-crown-6	THF	100	14
CsF/18-crown-6	benzene	92	29
RbF/18-crown-6	CH_2Cl_2	93	16
RbF/18-crown-6	THF	76	21
RbF/18-crown-6	benzene	100	21
KF/18-crown-6	CH_2Cl_2	52	75
KF/18-crown-6	THF	46	25
KF/18-crown-6	benzene	73	35
NaF/15-crown-5	THF	0	19
LiF/12-crown-4	THF	0	75
$KF{-}Al_2O_3$ [b]/18-crown-6	THF	1	24

[a] GLC data. [b] KF supported by Al_2O_3, ~ 5.5 mmol F^-/g.

Table 2

Hydrosilylation of carbonyl compounds **1** with dimethylphenylsilane catalysed by CsF/18-crown-6 (25 °C, the molar ratio **1**: $HSiMe_2Ph = 1:1.1$)

1 or **2**	Ar	R	Amount of catalysts (mol %)		Reaction time (h)	Isolated yield of **2** (%)	B.p. (°C/mmHg)	Anal. Found (calc.) (%)	
			CsF	18-crown-6				C	H
a	Ph	H	10	5	11	57	135–138/8 [a]	–	–
b	Ph	CH_3	10	5	7	54	115/2 [b]	–	–
c	2-furyl	H	10	10	3	67	105–106/2.7	65.98 (67.20)	6.92 (6.94)
d	5-methyl-2-furyl	H	10	5	0.5	58	117–118/6.5	67.81 (68.25)	7.66 (7.36)
e	5-trimethylgermyl-2-furyl	H	10	5	24	52	108–109/1.2	56.47 (55.06)	7.07 (6.93)
f	2-furyl	CH_3	13.4	6.7	10	61	93–94/4	68.22 (68.25)	7.43 (7.36)
g	5-methyl-2-furyl	CH_3	10	5	15	66	114–118/2.2	69.73 (69.19)	7.73 (7.74)
h	2-thienyl	H	10	5	3	54	110–115/1.5	62.64 (62.85)	6.72 (6.49)
i	2-thienyl	CH_3	5	2.5	11	45	136–138/3	64.27 (64.07)	6.83 (6.91)
j	3-thienyl	CH_3	5	5	10	53	110–111/1	63.44 (64.07)	7.38 (6.91)

[a] Lit. [16] b.p. 110–120 °C (bath temp.)/1 mmHg. [b] Lit. [16] b.p. 120–130 °C (bath temp.)/1 mmHg.

effectiveness of the catalytic pair CsF/18-crown-6 in the reactions of destannylation/alkylation [19], bromine to fluorine exchange [19], and isomerisation of silylhydrides [20] has also been demonstrated. It has been supposed [19] that the high activity of the CsF/18-crown-6 pair depends on the ability of caesium salts to form with 18-crown-6 1 : 2 or 2 : 3 complexes (sandwich or club sandwich) [18], although to our knowledge, complexes of alkali metal fluorides with 18-crown-6 in crystalline state have not been obtained so far. Study of the influence of the ratio of the components in catalytic system CsF/18-crown-6 on its activity in the hydrosilylation of 2-acetylpyridine with dimethylphenylsilane has favoured the suggestion about formation of sandwich complexes. It has been shown that a two-fold relative excess of 18-crown-6 drastically intensified the reaction [21]. High activity of RbF/18-crown-6 and CsF/18-crown-6 systems is evidently a consequence of the ability of the crown ether to solubilize these otherwise incompatible cations in form of highly lipophilic sandwich type complexes containing a "naked" fluoride ion inducing hydrosilylation of the C=O bond.

In the absence of a phase-transfer agent caesium fluoride is essentially inactive.

Sodium and lithium fluorides in the presence of 15-crown-5 and 12-crown-4, correspondingly, do not catalyse hydrosilylation of acetophenone. This is, obviously, connected with the low lipophilicity and non-solubility in the solvents studied of crown ether complexes of these fluorides.

The catalytic pair CsF/18-crown-6 (in CH_2Cl_2) was, as it is the most active, used for hydrosilylation of various aldehydes and ketones (mainly heterocyclic ones) (Table 2). Silyl ethers of corresponding aryl and heteryl carbinoles, the products of these reactions, were isolated in 45–67% yields. 1,1,3,3-Tetramethyl-1,3-diphenyldisiloxane results as a by-product in small amounts (1–5%) in practically all cases. The concentration of the disiloxane in reaction mixtures was, as a rule, higher when the reaction rate was lower.

Aldehydes were found to be somewhat more reactive than ketones. Reactivities of phenyl-, furyl-, and thienyl-containing aldehydes and ketones differ only insignificantly. Besides compounds **1a–j**, 5-trimethylsilylfurfural (**1k**), 2-pyrrolealdehyde (**1l**), 2-acetylpyrrole (**1m**), and 1-methyl-2-acetylpyrrole (**1n**) were treated with $HSiMe_2Ph$ in the presence of CsF/18-crown-6. In all cases only trace amounts of the corresponding **2k–n** were fixed by GLC-MS. In the case of **1k** the reaction mixture contained (after completion of reaction) a few products; the main product was **2c** which forms, obviously, as a result of the desilylation of starting **1k** followed by subsequent hydrosilylation of furfural. Pyrrole-containing compounds **1l–n** had very low reactivity under the conditions of these experiments.

Thus, fluoride ion-induced hydrosilylation of aldehydes and ketones can be successfully carried out in low-polarity media (CH_2Cl_2, benzene, THF) using freely available alkali metal fluorides (better CsF and RbF) as the F^- source and 18-crown-6 as the phase-transfer agent. This method of reduction of aryl and hetaryl aldehydes and ketones is considerably simpler, milder and more convenient than previously reported methods using expensive transition metal complexes as catalysts [22,23].

Experimental

^1H NMR spectra were recorded on a Bruker WH-90/DS (90 MHz) instrument using $CDCl_3$ as solvent and Me_4Si as internal standard. Mass spectra were reg-

Table 3

^{1}H NMR spectroscopy data for silyl ethers **2**

Compound	δ (ppm)
2c	0.37 (s, 6H, $Si(CH_3)_2$); 4.58 (s, 2H, CH_2); 6.1–6.3 (m, 2H, 3-H and 4-H); 7.2–7.7 (m, 6H, 5-H and C_6H_5)
2d	0.36 (s, 6H, $Si(CH_3)_2$); 2.22 (s, 3H, CH_3); 4.51 (s, 2H, CH_2); 5.7–6.1 (m, 2H, 3-H and 4-H); 7.2–7.7 (m, 5H, C_6H_5)
2e	0.36 (s, 6H, $Si(CH_3)_2$); 0.39 (s, 9H, $Ge(CH_3)_3$); 4.62 (s, 2H, CH_2); 6.13 (m, 1H, 4-H); 6.40 (m, 1H, 3-H); 7.2–7.7 (m, 5H, C_6H_5)
2f	0.31 (s, 3H, $SiCH_3$); 0.35 (s, 3H, $SiCH_3$); 1.36 (d, 3H, $J = 6$ Hz, $CHCH_3$); 4.82 (q, 1H, $J = 6$ Hz, OCH); 6.0–6.3 (m, 2H, 3-H and 4-H); 7.2–7.7 (m, 6H, 5-H and C_6H_5)
2g	0.33 (s, 3H, $SiCH_3$); 0.35 (s, 3H, $SiCH_3$); 1.45 (d, 3H, $J = 6.5$ Hz, $CHCH_3$); 2.23 (d, 3H, $J = 1$ Hz, CH_3 in furan ring); 4.79 (q, 1H, $J = 6.5$ Hz, $CHCH_3$); 5.83 (m, 1H, 4-H); 5.97 (m, 1H, 3-H); 7.2–7.7 (m, 5H, C_6H_5)
2h	0.39 (s, 6H, $Si(CH_3)_2$); 4.81 (d, 2H, $J = 0.4$ Hz, CH_2); 6.89 (m, 2H, 3-H and 4-H); 7.14 (m, 1H, 5-H); 7.2–7.7 (m, 5H, C_6H_5)
2i	0.33 (s, 3H, $SiCH_3$); 0.36 (s, 3H, $SiCH_3$); 1.49 (d, 3H, $J = 6.2$ Hz, $CHCH_3$); 5.06 (q, 1H, $J = 6.2$ Hz, $CHCH_3$); 6.84 (m, 2H, 3-H and 4-H); 7.11 (m, 1H, 5-H); 7.2–7.7 (m, 5H, C_6H_5)
2j	0.31 (s, 3H, $SiCH_3$); 0.36 (s, 3H, $SiCH_3$); 1.44 (d, 3H, $J = 6.4$ Hz, $CHCH_3$); 4.91 (q, 1H, $J = 6.4$ Hz, $CHCH_3$); 6.8–7.7 (m, 8H, thiophene protons and C_6H_5)

[a] Spectral parameters of **2a** and **2b** coincide with those described previously [16].

Table 4

Mass spectroscopy data for silyl ethers **2**

Compound	m/z (rel. abundance)
2c	242 (M^+, 22), 217 (12), 154 (19), 142 (17), 135 (23), 111 (48), 81 (100), 53 (60), 45 (36)
2d	246 (M^+, 26), 231 ($M^+ - CH_3$, 18), 168 (19), 153 (3), 137 (100), 95 (75), 75 (13), 43 (19)
2e	350 (M^+, 1), 231 (22), 199 (22), 181 (32), 157 (30), 135 (62), 119 (87), 95 (100), 43 (17)
2f	246 (M^+, 12), 231 (29), 168 (17), 137 (100), 95 (50), 91 (16), 75 (18), 65 (19), 51 (19), 45 (43)
2g	260 (M^+, 7), 245 ($M^+ - CH_3$, 57), 182 (15), 171 (20), 135 (100), 109 (62), 91 (13), 75 (12), 53 (11), 43 (48)
2h	248 (M^+, 5), 203 (19), 170 (45), 155 (15), 135 (20), 97 (100), 53 (10), 45 (17)
2i	262 (M^+, 10), 247 (24), 184 (53), 169 (12), 137 (100), 111 (37), 75 (15), 45 (27)
2j	262 (M^+, 10), 247 (14), 188 (11), 173 (13), 137 (100), 111 (20), 75 (25), 45 (22)

istered on a MS-25 spectrometer (Kratos, 70 eV). GLC analysis was conducted on a Chrom-5 instrument equipped with a flame-ionization detector using a glass column (1.2 m × 3 mm) packed with 5% OV-17 on Chromosorb W-HP (80–100 mesh). Helium (60 cm^3/min) was used as carrier gas, analysis temperature was 150–175 °C depending on reaction mixture. Commercially available aldehydes and ketones **1a–d**, **f–j** were used. Aldehyde **1e** was prepared as previously described [24]. All carbonyl compounds were distilled *in vacuo* prior to use. Dichloromethane, benzene and THF were purified as previously described [25]. Alkali metal fluorides were calcinated at ~ 350 °C prior to use. 18-Crown-6 was dried in a vacuum desiccator over P_2O_5.

Hydrosilylation of acetophenone with dimethylphenylsilane. General procedure for the reaction of acetophenone with dimethylphenylsilane on semi-micro scale

Acetophenone (0.187 ml, 1.6 mmol), dimethylphenylsilane (0.274 ml, 1.76 mmol), solvent (1.6 ml), freshly calcinated alkali metal fluoride (0.16 mmol) and crown ether (0.08 mmol) were placed in a Pierce reacti-vial (5 ml). The reaction mixture was stirred at room temperature with reaction course control (GLC). Content of hydrosilylation product was determined using an absolute calibration method. The results are summarized in Table 1.

Hydrosilylation of aldehydes and ketones 1a–j (general procedure)

18-Crown-6 and freshly calcinated caesium fluoride (for concentrations of both these catalysts, see Table 2) were added to a solution of carbonyl compound (16 mmol) and dimethylphenylsilane (17.6 mmol) in dry dichloromethane (16 ml). The mixture was stirred at room temperature (GLC-control; for reaction times, see Table 2), filtered and CH_2Cl_2 was evaporated under reduced pressure. Distillation of the residue in vacuo affords silyl ethers **2** (see Table 2). ^1H NMR and mass spectroscopy data of previously unknown compounds are given in Tables 3 and 4.

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