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Preliminary communication

Fluoride ion-induced hydrosilylation of aldehydes and ketones under phase-transfer conditions

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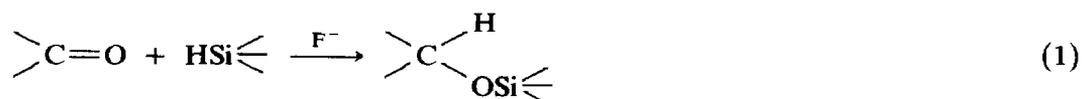
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Abstract

The hydrosilylation of aldehydes and ketones with dimethylphenylsilane occurs readily in dichloromethane at room temperature in the presence of catalytic amounts of caesium fluoride and 18-crown-6 to afford silyl ethers of the corresponding aryl and hetaryl carbinols in good yields.

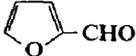
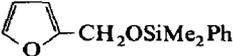
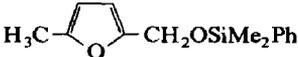
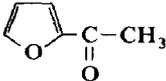
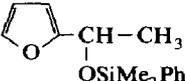
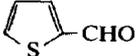
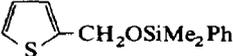
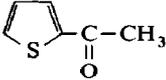
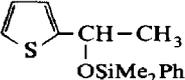
Fluoride ion-induced hydrosilylation of carbonyl compounds (aldehydes, ketones, esters) by various hydrosilanes (eq. 1) has been known for some time [1–6]. The reaction is carried out without solvent [2–4,6] or in aprotic polar solvents (MeCN, DMFA, DMSO) [1,5,6], the alkali metal fluorides (mainly CsF and KF) being the usual source of fluoride ions.



The hydrosilane/F⁻ system, as previously described in refs. 1–6, has not been widely applied in organic synthesis, obviously because it requires at least stoichiometric amounts of metal fluoride, heterogeneous and sometimes drastic reaction conditions. Fujita and Hiyama [7,8] have studied reaction 1 in detail and have found that the hydrosilylation of aldehydes and ketones with dimethylphenylsilane (and with some other hydrosilanes) can be successfully carried out in hexamethylphosphoric triamide (HMPA) in the presence of catalytic amounts of tetrabutylammonium fluoride (tris(diethylamino)sulphonium difluorotrimethylsilicate can also serve as a source of F⁻). The catalyst Bu₄N⁺F⁻ is essentially inactive in CH₂Cl₂ or THF, moreover CsF in HMPA was substantially less active than Bu₄N⁺F⁻ [8]. High yields of the hydrosilylation products in the system HMPA/Bu₄N⁺F⁻/HSiR₃ were achieved only in the case of aldehydes. The limitations of the method as described elsewhere [7,8] are also connected with the laborious and time-consuming procedure used to prepare the anhydrous Bu₄N⁺F⁻ and with the difficulties associated with the preparative isolation of products from HMPA (preparative GLC was used [8]).

Table 1

Hydrosilylation of aldehydes and ketones with dimethylphenylsilane in dichloromethane in the presence of CsF and 18-crown-6 ^a

Aldehyde or ketone	Reaction time (h)	Product	Isolated yield (%)
PhCHO	11	PhCH ₂ OSiMe ₂ Ph	57
$\text{Ph}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$	7	$\text{Ph}-\underset{\text{OSiMe}_2\text{Ph}}{\underset{ }{\text{CH}}}-\text{CH}_3$	54
	3		67
	0.5		58
	10		61
	3		54
	11		45

^a Reaction conditions: room temperature, the molar ratio of aldehyde (or ketone) : HSiMe₂Ph : CsF : 18-crown-6 = 1 : 1.1 : 0.1 : 0.05

We have found that the hydrosilylation of aromatic and heteroaromatic aldehydes and ketones proceeds readily at room temperature 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. Under these extremely mild conditions, silyl ethers of the corresponding aryl and hetaryl carbinols are formed in good yields (without optimization) (Table 1). The products can be readily isolated from the reaction mixtures by vacuum distillation. The disiloxane Me₂PhSiOSiPhMe₂ is formed as a by-product in small quantities (1–5%). The reaction is very simple to realize and is exemplified by a typical procedure for the hydrosilylation of 2-acetylfuran.

To a solution of 2-acetylfuran (2.64 g, 24 mmol) and dimethylphenylsilane (4.11 ml, 26.4 mmol) in dry dichloromethane (20 ml) was added 18-crown-6 (0.42 g, 1.6 mmol) and freshly calcinated caesium fluoride (0.48 g, 3.2 mmol). The mixture was stirred for 10 h at room temperature. After completion of the reaction (monitoring by GLC) the solids were filtered off, the solvent was evaporated under reduced pressure, and the residue was distilled in vacuo to give 3.6 g (61%) of dimethylphenyl[1-(2-furyl)ethoxy]silane, b.p. 93–94°C/4 mmHg; ¹H NMR spectrum (90 MHz, CDCl₃/TMS), δ (ppm): 0.31 (s, 3H, SiCH₃), 0.35 (s, 3H, SiCH₃), 1.36 (d, 1H, *J* = 6 Hz, CHCH₃), 4.82 (q, 1H, *J* = 6 Hz, OCH), 6.0–6.3 (m, 2H, furan 3-H and 4-H), 7.2–7.7 (m, 6H, furan 5-H and C₆H₅); mass spectrum, *m/z* 246 (*M*⁺); Anal. found: C 68.22, H 7.43, calculated for C₁₄H₁₈O₂Si: C 68.25, H 7.36%.

The hydrosilylation of the other carbonyl compounds (see Table 1) was carried

out similarly. The structure of obtained compounds obtained was confirmed by ^1H NMR and mass spectroscopy data.

In the absence of phase-transfer agents the hydrosilylation scarcely takes place. Thus, when acetophenone was allowed to react with dimethylphenylsilane in CH_2Cl_2 in the presence of CsF for 24 h, only traces ($< 1\%$) of dimethylphenyl(1-phenylethoxy)silane were detected in the reaction mixture and after 6 days the reaction mixture contained ca. 5% of this product. Since various heterogeneous reactions, including phase-transfer ones, can be successfully carried out under sonication [9,10], we have checked the possibility of using sonolysis during fluoride ion-induced hydrosilylation in the absence of phase-transfer agents, i.e. under heterogeneous conditions. Experiments show that the reaction can be considerably accelerated by ultrasonication: sonolysis of a mixture of PhCOCH_3 , PhMe_2SiH and CsF (10 mol.%) in CH_2Cl_2 for 24 h (Branson[®] B-52 ultrasonic cleaning bath, 250 W, 45 kHz) affords $\text{PhCH}(\text{OSiMe}_2\text{Ph})\text{CH}_3$ in ca. 20% yield (GLC data).

Thus, fluoride ion-induced hydrosilylation of aldehydes and ketones proceeds readily in low-polarity medium in the presence of crown ether as phase-transfer agent. At present, these reactions are being studied by us in an attempt to elucidate the influence of the nature of the solvent, the metal fluoride and phase-transfer agent on the process in order to determine the scope and limitations of the method. The results are to be published elsewhere.

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