Acylsilanes and *C*-Stannylimines as Anion Equivalents

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Summary Acylsilanes and *C*-stannylimines react with organic halides in the presence of KF–18-crown-6 ether to give ketones and ketimines, respectively.

Acylsilanes are known to react with aqueous tetrahydrofuran (THF)[1,2] to give the corresponding aldehydes in high yield [equation (1)] and so we wished to evaluate the potential of these and allied substrates as acyl and related anion equivalents (umpolung concept). We describe here the results of our initial investigations.

$$\mathrm{ArCOSiMe_3 + H_2O \xrightarrow[THF]{} ArCHO} \qquad (1)$$

In the presence of KF and a catalytic quantity of 18-crown-6 ether (10 mol%), benzoyl(trimethyl)silane (**1**) reacts at elevated temperatures with a range of organic halides to give modest yields of ketones, together with variable amounts of benzil [Table 1, equation (2)].

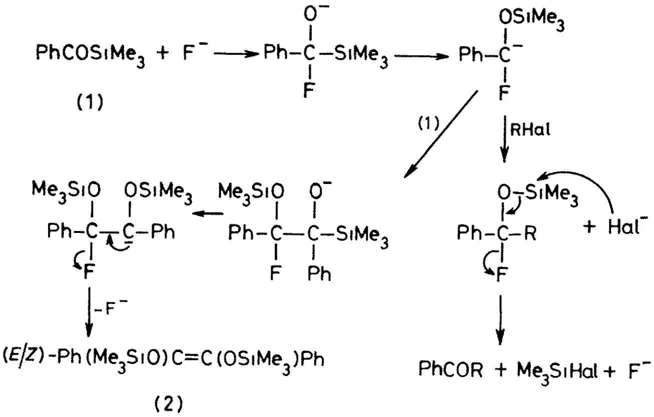
Table 1. Ketones, PhCOR, prepared from $PhCOSiMe_3$ and RHal in the presence of KF–18-crown-6.[a]

RHal	PhCOR/%[b]	PhCOCOPh/%	Reaction conditions[c]
$PhCH_2Br$	90	—	A
$PhCOCH_2Br$	30	25	B
$CH_2{=}CHCH_2Br$	25[d]	30	A,B
MeI	30	20	B

[a] $PhCOSiMe_3$–KF–18-crown-6 1 : 3 : 0·1. [b] Yield based upon $PhCOSiMe_3$ consumed. [c] A; 3 h, 160 °C, mesitylene: B; 16 h, 80 °C, THF. [d] $PhC(OH)(COPh)CH_2CH{=}CH_2$ (*ca.* 20% also obtained.

$$\underset{(\mathbf{1})}{\mathrm{PhCOSiMe_3}} + \mathrm{RHal} \rightarrow \mathrm{PhCOR} + \mathrm{PhCOCOPh} \qquad (2)$$

Neither ketone nor benzil are formed if the crown ether is omitted and the reaction is not influenced by the addition of dibenzoyl peroxide, from which we conclude that homolysis of the acyl–silicon bond cannot play a significant role Interestingly, if the organic halide is omitted, (**1**) reacts with itself in the presence of KF–18-crown-6 (3 h at 160 °C in mesitylene) to give (*E*/*Z*)-Ph(Me_3SiO)C=C($OSiMe_3$)Ph † (**2**) (70%), which on prolonged treatment with the catalyst system, is converted into benzil and hexamethyldisilane No trace of (**2**), however, could be detected in reactions involving organic halides



SCHEME

The reactions can be rationalised in the Scheme, based upon the mechanism first advanced by Brook *et al* [1] to account for the solvolysis This new ketone synthesis complements the masked-anion approach in which lithium di-isopropylamide is used to abstract a proton from RCH($OSiMe_3$)CN species (prepared from Me_3SiCN and RCHO) [3]

C-Trimethylstannylimines, *e g* Ph(Me_3Sn)C=NPh (conveniently prepared from PhCCl=NPh and Me_3SnLi),[4] react in an analogous fashion with organic halides to give the corresponding ketimines [Table 2, equation (3)] Again KF–18-crown-6 is essential for the reaction to occur From ancillary kinetic studies[5] we conclude that in this case, the initial fluoride-ion attack takes place on tin with generation of the *C*-imino-anion equivalent, rather than at carbon with subsequent migration of the trimethylstannyl group from carbon to nitrogen

TABLE 2 Imines, PhRC=NPh, prepared from Ph(Me_3Sn) C=NPh and RHal in the presence of KF–18 crown-6 [a]

RHal	PhRC=NPh/% [b]	RHal	PhRC=NPh/% [b]
$PhCH_2Br$	40	CH_2=$CHCH_2Br$	20
$PhCOCH_2Br$	35	MeI	30
PhCOCl	35		

[a] Table 1, conditions B [b] Yield based upon Ph(Me_3Sn) C=NPh consumed Accompanied by traces of PhCH=NPh derived from the unreacted starting material which is hydrolysed during the work up

$$\text{Ph(Me}_3\text{Sn)C=NPh} + \text{RHal} \rightarrow \text{PhCR=NPh} + \text{Me}_3\text{SnHal} \quad (3)$$

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† Identical with a specimen prepared by an alternative route (V Schrapler and K Ruhlmann, *Chem Ber* , 1963, **96**, 2780).

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