REACTION OF ENAMINOSILANE. SELECTIVE C-ACYLATION OF
ENAMINOSILANES WITH ACID CHLORIDES.

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Summary: In the presence of potassium fluoride and crown ether, acyl groups are
introduced into the α-position of a imino group by acylation of enaminosilanes
in good yields.

It is generally quoted that the reaction of metal enolates with acylating reagents is not
a practical methods of preparing of 1,3-dicarbonyl compounds.[1] The silyl derivatives of ester
(ketene silyl acetals) are readily C-acylated with acid chlorides to give β-keto esters.[2]
The less reactive silyl enol ethers, however, are only C-acylated with polyhalogenated acid
chlorides.[3] Simple acid chlorides either do not react or, in the presence of murcury(II)
chloride[4], react to give exclusively O-acylated products. Recently, Rathke reported the first
selective C-acylation of silyl enol ethers with acetyl tetrafluoroborate to afford 1,3,-
diketones in reasonable yields.[5]

We would like to report here that enaminosilanes, which are nitrogen-analogues of silyl
enol ethers, react readily with simple acid chlorides in the presence of potassium fluoride
and a catalytic amount of crown ether under mild conditions to afford β-keto imines in good
yields.
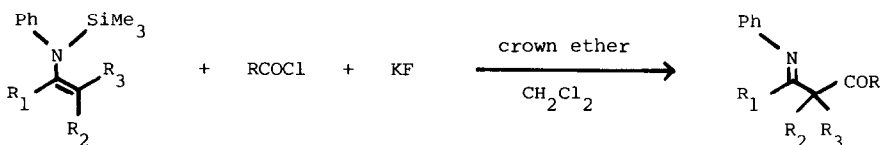
In a typical C-acylation procedure, to a solution of dry potassium fluoride (174 mg, 3mmol),
dicyclohexyl-18-crown-6-ether (5mol%) in anhydrous dichloromethane (2.5 ml) was added ethyl
chloroformate (325 mg, 3mmol), and then N-cyclohexenylanilinotrimethylsilane(1) (490 mg, 2mmol)
by a syringe at room temperature under a nitrogen atmospher. After stirring for 10 hr, examina-
tion of the reaction mixture by GLC indicated that 2-ethoxycarbonylcyclohexylideneaniline was
formed in quantitative   yield as the only product. The reaction mixture was quenched with 10 ml
of water, and extracted with ether. Isolated yield by column chromatography on silica gel was
a 84% (412 mg) yiels.

In a similar mannar, a variety of enaminosilanes was examined as summarized in Table 1. In all cases the yields of β-keto imines were nearly quantitatively. The regiochemistry of the C-acylation was examined with N-(6-methylcyclohexenyl)anilinotrimethylsilane(3) obtained from 2-methylcyclohexylideneaniline under kinetic-controlled conditions. In this case, the acyl group was smoothly introduced regiospecifically to afford only a single C-acylated product, and no detectable contamination (GLC and NMR analysis) of the regioisomeric product was observed.

Similarly, acylation was extended for silyl enol ether, such as cyclohexanone silyl enol ether, instead of enaminosilane, with benzoyl chloride. Unfortunately, no C-acylated product was obtained, and only a exclusive formation of cyclohexanone enol benzoate was obseved in 88% yield. This O-acylated result is strikingly similar to those observed by Olofson[6] in the reaction of acid chloride and silyl enol ether in the presence of a catalytic amount of tetraalkylammonium fluoride.

In sharp contrast, when the same reactions were carried out with benzoyl chloride or benzoyl fluoride in the absence of crown ether and/or potassium fluoride, benzanilide and cyclohexanone were the main products and the formation of the desired β-keto imines could not be detected.

These results suggest that apparently fluoride ion which has a strong affinity to silicon atom serves as the important role. There is no direct evidences for the intermediacy of free anion of type (B) generated from cleavage of enaminosilane by fluoride ion; the anionic hypervalent enamonosilane (A) may well be the reactive species. Such anion (B) undergoes C-acylation owing to an unfavorable equilibrium position (Scheme 1).
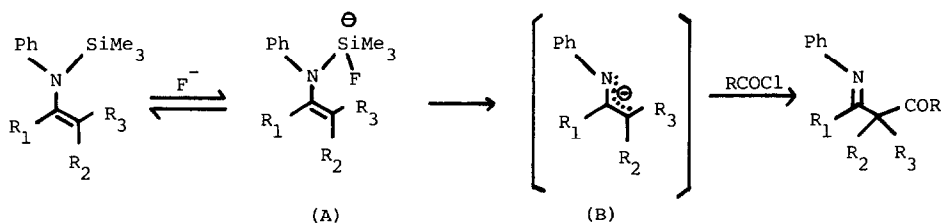
Scheme 1

In the absence of fluoride ion, N-acylation appears to proceed with predominant the amide formation followed by hydrolysis to afford benzanilide and the corresponding ketone (Scheme 2).
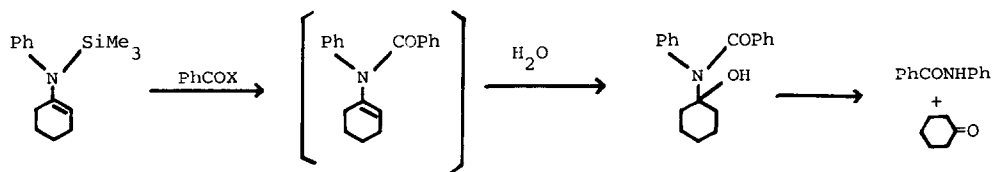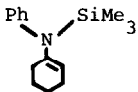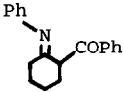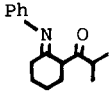

Scheme 2

Table 1
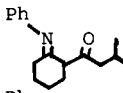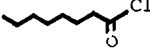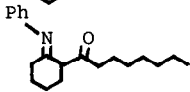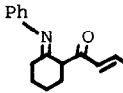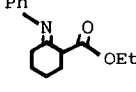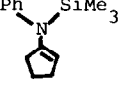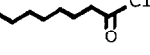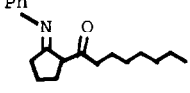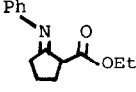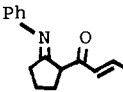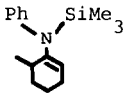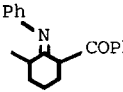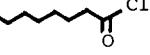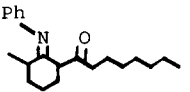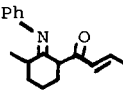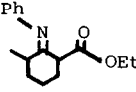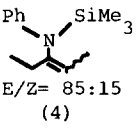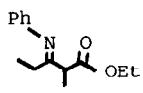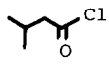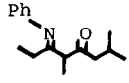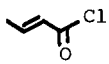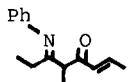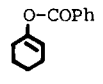
entry	enaminosilane	acid chloride	reaction conditions	product[a]	yield(%)[b]
1	(1)	PhCOCl	r.t./3 hr		90
2	(1)		0°/30 min then r.t./2.5 hr		93
3	(1)		0°/20 min then r.t./1.5 hr		89
4	(1)		r.t./1 hr		92
5	(1)		r.t./3 hr		81
6	(1)	ClCOOEt	r.t./10 hr		84
7	(2)		r.t./2 hr		82
8	(2)	ClCOOEt	r.t./2 hr		88
9	(2)		0°/30 min then r.t./2 hr		71
10	(3)	PhCOCl	r.t./6 hr		94
11	(3)		r.t./2 hr		89
12	(3)		r.t./2 hr		62
13	(3)	ClCOOEt	r.t./3 hr		98

Table 1 / continued

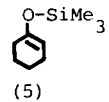| entry	enaminosilane	acid chloride	reaction conditions	product[a]	yield(%)[b]
14	Ph—SiMe$_3$ on N, E/Z= 85:15 (4)	ClCOOEt	0°/2 hr	Ph, N O OEt	84
15	(4)	Cl (O)	0°/1.5 hr	Ph, N O	79
16	(4)	Cl (O)	r.t./1 hr	Ph, N O	76
17	O-SiMe$_3$ (5)	PhCOCl	r.t./18 hr	O-COPh	88
18	(1)	PhCOCl	reflux/20 hr[c]	PhCONHPh (+ ◯=O)[d]	66
19	(1)	PhCOF	reflux/5 days[c]	PhCONHPh (+ ◯=O)[d]	79

a) The β-keto imine form is shown although most products are mixture of carbonyl and
    enol form (by IR and NMR analysis).

b) Isolated yields of chromatographed or recrystallized products.

C) The reaction was carried out in the absence of crown ether and potassium fluoride.

d) Cyclohexanone was detected by GLC analysis.

References and Note.

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    (b) J.K.Rasmussen, Synthesis, 819 (1977).

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