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FLUORIDE ION INDUCED REACTIONS OF ORGANOSILANES WITH SATURATED LACTONES AND $\alpha\beta$-ENONES

Alfredo Ricci*, Mariella Fiorenza, M.Antonietta Grifagni, and Giuseppe Bartolini
Centro di Studio sulla Chimica e la struttura dei Composti Eterociclici e loro applicazioni del CNR c/o Istituto di Chimica Organica dell'Università, Via G.Capponi 9, Firenze(Italy).

Giancarlo Seconi
Istituto dei Composti del Carbonio contenenti eteroatomi e loro applicazioni del CNR, Via Tolara di Sotto 89,Ozzano-Emilia, Bologna (Italy).

Summary. Benzyl-, heteroaryl-, and allylsilanes, under the catalytic action of CsF or silica/TBAF, react in mild conditions with electrophiles such as δ-valero and ε-caprolactone, and with cyclohexen-2-one

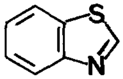
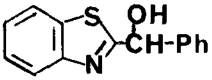
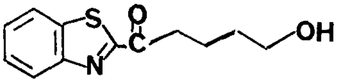
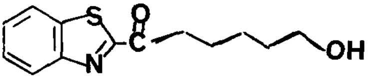
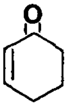
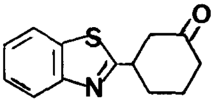
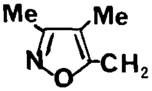
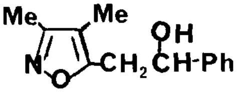
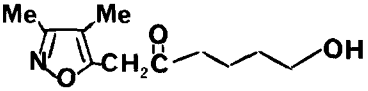
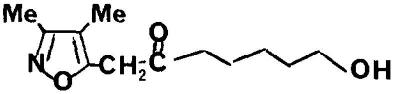
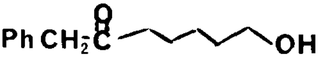
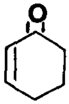
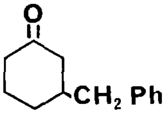
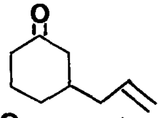
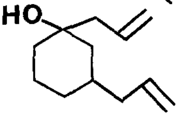
The easy F^--catalysed desilylation of organosilicon compounds containing a C-SiR_3 bond has now been developed into a general method for the transfer of acyl[1], alkynyl[2], benzyl[3], allyl[4] and oxiranyl[5] carbanions to an electrophilic centre. However, in spite of the large number of papers in this field, this synthetic methodology has been applied with very few exceptions[3,4] only to aldehydes and ketones as electrophiles

We have found that the transfer of benzyl- and heteroaryl carbanions, generated from the corresponding organosilanes, can be extended to a wider range of electrophiles such as saturated lactones or $\alpha\beta$-enones, containing an electrophilic carbon, to give compounds otherwise relatively inaccessible.

All the reactions were run under argon at various temperatures, and catalytic amounts of CsF or silica-supported tetrabutylammonium fluoride (TBAF/SiO_2), were sufficient to drive the reactions. Details of these reactions together with the data related to PhCHO as standard electrophile are given in the Table.

δ-Valerolactone (δ-V-L) and ε-caprolactone (ε-C-L) reacted smoothly with various representative organosilanes with cleavage of the acyl-oxygen bond affording the corresponding ketoalcohols in reasonably good yields. All attempts at in-

Table F^- catalysed reaction of organosilanes with electrophiles.

Entry	R in R-$SiMe_3$	Catalyst	Electrophile	Product[b]	(% yield)[a]
1		CsF;TBAF/SiO_2	PhCHO		(90)
2		"	δ-V-L		(60)
3		"	ε-C-L		(65)
4		"			(50)
5		"	PhCHO		(80)
6		"	δ-V-L		(45)[c,d]
7		"	ε-C-L		(55)
8	$PhCH_2$	"	PhCHO	$PhCH_2CH(OH)Ph$	(85)
9		"	ε-C-L		(35)[c,d]
10		TBAF/SiO_2			(48)[d]
11		CsF	"		(65)
12		TBAF/SiO_2	"		(60)

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[a] Unless otherwise stated the yields are of isolated products.

[b] All the new products were characterized by spectral means

[c] Gas-cromatographic yields.

[d] Reaction performed in refluxing THF.

ducing the reaction of β-propiolactone with a carbanion failed because of ring opening and polymerisation,[6] whereas γ-butyrolactone (not quoted in the Table), gave only modest conversion yields[7] ($<15\%$ as estimated by GC/MS analysis). No reaction was observed between lactones and allylsilane.

With cyclohexen-2-one as an electrophile, conjugate addition of allyl-, benzyl-, and benzothiazolyl carbanions occurred with formation of the Michael adduct (entries 4, 10, 11). As shown in the Table the yields of the reactions with the new electrophiles were generally lower than those with PhCHO.

Several aspects of these reactions are noteworthy: they provide the first instance of regioselective opening of the ring of a saturated lactone by Group IV B organometallics with formation of a new carbon-carbon bond[8], through attack of a carbanion on the hard centre of the ring system. In the conjugate addition to $\alpha\beta$-enones, the F^- based procedure offers an alternative to the Lewis acid catalysed procedure[9] for the more reactive systems, and opens a unique prospect to Michael-type additions, starting from relatively unreactive organosilanes, corresponding to weak carbon acids R-H(entry 8). Moreover the regioselectivity in the reaction of the allylsilane with an $\alpha\beta$-enone, appears to depend on the cata lyst: in fact when TBAF/SiO_2 was used as catalyst, conjugate addition took place along with 1-2 addition of the allyl carbanion, affording the product of double allylation (entry 12), whereas with CsF, only the expected product of conjugate addition was formed.

Preparation of (3) illustrates the standard procedure: To 0.11 g (0.72 mmol) of dry CsF in 5 ml dry tetrahydrofuran (THF) was added drpwise a solution of 2-trimethylsilylbenzothiazole (1.5 g, 7.2 mmol) and ε-C-L (0.82 g, 7.2 mmol) in 3 ml dry THF. The pale yellow solution was stirred overnight at room temperature After evaporation of the THF, the resulting dark orange oil was hydrolysed with acidic water and extracted with ether. The solvent was evaporated and the residue was purified by distillation under high vacuum, affording 1.15 g (65%) of 3 (b.p. 160°/0.6 mm Hg)

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8. To our knowledge the only reports concerning reactions of saturated lactones with organometallics refer to the complex and not regiospecific interaction of Grignard reagents with β-propiolactone: J. F. Normant, A. Alexakis and G. Cahiez, Tetrahedron Lett.,935 (1980) and references cited therein.

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