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FLUORIDE ION INDUCED REACTIONS OF ORGANOSILANES: THE PREPARATION OF MONO AND DICARBONYL COMPOUNDS FROM β-KETOSILANES

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Summary: β-ketosilanes react with a variety of carbon electrophiles in the presence of CsF to give mono- and dicarbonyl derivatives in reasonably good yields.

As a part of our continuing interest[1] in the synthetic utility of organosilanes we report here on a general method for the transfer of an $ArCOCH_2^-$ framework to an electrophilic centre, which outlines a new way for the synthesis of a variety of mono- or α,γ and α,δ-dicarbonyl compounds, some of them not readily accessible using conventional routes. This method (equation 1) is based on the high reactivity of the aromatic β-ketosilanes with a variety of carbon electrophiles under the catalytic action of F^- ions.

$$C_6H_5COCH_2SiMe_3 \xrightarrow[(F^-)]{E} C_6H_5COCH_2E \qquad \text{eqn. 1}$$

All the reactions were run under inert atmosphere and at room temperature owing to the easy thermal rearrangement of the β-ketosilanes to the corresponding silyl enol ethers[2]. The reactions with the various electrophiles proceeded smoothly with reasonably good yields and appeared regioselective. Stoichiometric amounts of CsF were used for driving the reactions. Details of these reactions are given in the Table.

In addition to the usual carbonyl derivatives, organic bromides were shown to interact with β-ketosilanes and also noteworthy is the use of α-ketosilanes as electrophiles. Changing the catalytic species did not prove to be particularly useful in that neither TBAF or 18-crown-6/KF complex improved to a sizeable extent the yields of the reactions. Only in the case of cyclohexenone (entry 2 in the Table) the use of TBACN (Tetrabutylammonium cyanide) resulted, in agreement with a recent observation[3], in a large increase of the rate of the reaction.

TABLE. Reactions of $C_6H_5COCH_2SiMe_3$ with electrophiles in THF, catalysed by CsF.

Entry	Electrophile	Product	Reaction time, h	Yields[a] %
1	PhCHO	$PhCOCH=CHPh$[b]	4	90
2	$CH_2CH_2CH_2CH=CHCO$	$PhCOCH_2CHCH_2CH_2CH_2COCH_2$[b]	6	80[c]
3	$PhCH_2Br$	$PhCOCH_2CH_2Ph$	12	70
4	$CH_2=CHCH_2Br$	$PhCOCH_2CH_2CH=CH_2$ + $PhCOCH(CH_2CH=CH_2)_2$	15	30 + 30
5	$PhCOCH_2Br$	$PhCOCH_2CH_2COPh$	16	40
6	$PhCOSiMe_3$	$PhCOCH=CHPh$ + $PhCOCH_2COPh$	8	20 + 40[d]
7	2-Furyl$COSiMe_3$	2-Furyl$CH=CHCOPh$ + 2-Furyl$COCH_2COPh$	2	10[d] + 40[d]

[a] Unless otherwise stated the yields are of isolated products. [b] See footnote 4. [c] With TBACN in THF: reaction time 10', yield 80%. [d] Gas-chromatographic yield.

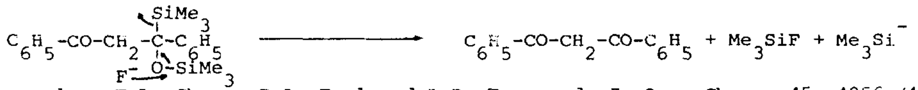
Acetophenone was recovered as a by-product in all the reaction investigated and products of double functionalisation were also formed in sizeable amounts (entry **4**) most likely through proton abstraction by the F^- ion from the product of monofunctionalisation followed by interaction of this carbanion with a second molecule of electrophile[5]. Interestingly in the reactions between α and β-ketosilanes the main products (entries **6** and **7**) were α,γ-diketones, the chalcones being formed only in minor amounts[6].

Preparation of **3** illustrates the standard procedure:

to 0.75 g (5.2 mmol) of dry CsF in 3 ml of dry THF was added dropwise a solution of β-ketosilane (1.0 g, 5.2 mmol) and benzyl bromide (0.89 g, 5.2 mmol) in 3 ml dry THF. The pale yellow solution was stirred overnight at room temperature. After evaporation of the THF, the resulting oil was hydrolysed with water and extracted with ether. The solvent was evaporated and the residue crystallised from alcohol, affording 0.76 g of **3** (m.p. 67-69°C).

REFERENCES AND FOOTNOTES

1. A. Ricci, M. Fiorenza, M.A. Grifagni, G. Bartolini and G. Seconi, Tetrahedron Lett., 5079 (1982) and references cited therein.
2. I.F. Lutsenko, Yu.I. Baukov, O.V. Dudukina and E.N. Kramarova, J. Organometal. Chem., 11, 35 (1968).
3. A. Ricci, A. Degl'Innocenti and A. Mordini, unpublished results.
4. Products of entry **1** and **2** have been also prepared starting from the silyl enol ether with CsF as catalyst; see J. Boyer, R.J.P. Corriu, R. Perz and C. Reye, J. Organometal. Chem., 184, 157 (1980).
5. Minor amounts of $(C_6H_5CO)_3CH$ were also formed in the reaction between α and β-ketosilanes.
6. Most likely formation of α,γ-diketones occurs through F^--catalysed desilylation of the following bis-silylated derivative, detected (GC/MS) during the reaction:



$$C_6H_5\text{-CO-}CH_2\text{-}\overset{SiMe_3}{\underset{O\text{-}SiMe_3}{C}}\text{-}C_6H_5 \xrightarrow{\quad} C_6H_5\text{-CO-}CH_2\text{-CO-}C_6H_5 + Me_3SiF + Me_3Si^-$$

see also: F.L. Chung, R.A. Earl and L.B. Townsend, J. Org. Chem., 45, 4056 (1980).

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