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FLUORIDE ION INDUCED REACTIONS OF ORGANOSILANES WITH ELECTROPHILES

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Summary: Benzyl- 4-picolyl- and phenylallyl(trimethyl)silanes react with electrophiles in the presence of KF/18-crown-6 or silica-TBAF under mild conditions.

Fluoride ion is known to display a marked nucleophilic affinity for silicon in organosilanes[1] due to the high Si-F bond energy, and this fact has been used to cleave X-Si bonds[1]. The proposed intermediacy of functionalized carbanions in F^- induced reactions, already reported for acyl[2], alkynyl[3], allyl[4] and oxiranyl[5] silanes, supports the contention that suitable organosilicon compounds containing a $C\text{-}SiR_3$ moiety can be considered as masked carbanions, which can be generated under relatively mild conditions, provided a suitable catalyst is present.

In this Letter, we describe the transfer of benzyl-, 4-picolyl- and phenylallyl- groups from the corresponding labile organosilanes to various weak electrophiles in the presence of KF/18-crown-6 or silica-supported tetrabutylammonium fluoride (silica-TBAF). Details are given in the Table. Reactions are rapid and high-yielding.

Table. F^- catalysed reactions of organosilanes with electrophiles[a]

R in $R\text{-}SiMe_3$	Electrophile	Product[b]	Yield (%)
$o\text{-}O_2NC_6H_4CH_2$	PhCHO	$o\text{-}O_2NC_6H_4CH_2CH(OH)Ph$	70
	$PhCH_2Br$	$o\text{-}O_2NC_6H_4CH_2CH_2Ph$	60
$3,5\text{-}Cl_2C_6H_4CH_2$	PhCHO	$3,5\text{-}Cl_2C_6H_4CH_2CH(OH)Ph$	70
	$PhCH_2Br$	$3,5\text{-}Cl_2C_6H_4CH_2CH_2Ph$	50
4-Picolyl	PhCHO	4-picolylCH(OH)Ph	80
	$PhCH_2Br$	4-picolylCH_2CH_2Ph	70
	$\mathrm{Me\overline{CHCH_2O}}$	4-picolylCH_2(OH)Me	30[c]
$PhCH{=}CHCH_2$	PhCHO	$PhCH{=}CHCH_2CH(OH)Ph$	50
	$PhCH_2Br$	$PhCH{=}CHCH_2CH_2Ph$	40

[a] THF, 12h, 20°, 10 mol% catalyst, under argon.
[b] Accompanied by small amounts (<10%) of RH. Product obtained after treating the reaction mixture with dilute HCl.
[c] Low yield due to competing F^- catalysed opening of the oxirane ring[6].

Organosilanes corresponding to carbon acids, RH, with pK_a <37 (Ref 7) appear therefore to be effective agents for transfering the organic group, R, to an electrophilic centre. A recent report[8)] on the other hand suggests that even this pK_a value may not be limiting.

The method described above is of preparative advantage in those cases where more reactive organometallic reagents cannot be used, *e.g.* with nitro-substituted or with pyridine-type derivatives. Products resulting from allyl-type rearrangements (leading to *o*-substituted toluenes) commonly encountered in Grignard reactions are also absent.

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REFERENCES

1. E. Colvin, Silicon in Organic Synthesis, Butterworth, 1981, chs 7-9.
2. A. Degl'Innocenti, S. Pike, D.R.M. Walton, G. Seconi, A. Ricci and M. Fiorenza, J.Chem.Soc.Chem.Commun., 1201 (1980).
3. E. Nakamura and I. Kuwajima, Angew.Chem.Internat,Edit., 8, 498 (1976); A.B. Holmes, C.L.D. Jennings-White, A.H. Schulthess, B. Akinde and D.R.M. Walton, J.Chem.Soc.Chem.Commun., 840 (1979).
4. A. Hosomi, A. Shirahata and H. Sakurai, Tetrahedron Lett., 3043 (1978).
5. T.H. Chan, P.W.K. Lan and M.P. Li, Tetrahedron Lett., 2667 (1976).
6. A. Rosowsky in A. Weissberger (Ed.), The Chemistry of Heterocyclic Compounds, 19 (Pt 2), ch 1 (1964); J.G. Buchanan and H.Z. Sable in B.S. Thyagarajan (Ed.), Selective Organic Transformations, Wiley, 1972, vol 2, p 1.
7. C. Eaborn, D.R.M. Walton and G. Seconi, J.Chem.Soc.Chem.Commun., 937 (1975); C. Eaborn, I.D. Jenkins and G. Seconi, J.Organometal.Chem., 131, 387 (1977); A. Fischer, M.W. Morgan and C. Eaborn, J.Organometal.Chem., 136, 323 (1977).
8. F. Effenberger and W. Spiegler, Angew.Chem.Internat.Edit., 20, 265 (1981).

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