

Selective Reduction of Carbonyl Compounds by Heterogeneous Catalysis on Salt Surfaces

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Summary $(\text{EtO})_3\text{SiH}$ and $\text{Me}(\text{EtO})_2\text{SiH}$ activated by KF and CsF are efficient and selective agents for the heterogeneous reduction of carbonyl groups.

WE report a new, practical, and highly selective method for the reduction of carbonyl compounds, using salts as heterogeneous catalysts. $(\text{EtO})_3\text{SiH}$ and $\text{Me}(\text{EtO})_2\text{SiH}$, easily obtainable from the industrially available Cl_3SiH and

MeCl_2SiH , are excellent reducing agents when activated by KF or CsF in the absence of solvent. $(\text{EtO})_3\text{SiH}$ activated by KF reduces aldehydes quantitatively with 100% selectivity in the following equimolar mixtures of aldehydes and ketones:† $\text{PhCHO} + \text{PhCOMe}$ (36 h reaction time); $\text{Me}[\text{CH}_2]_5\text{CHO} + \text{PhCH}_2\text{COCH}_2\text{Ph}$ (7 h); $\text{PhCHO} + \text{Bu}^t\text{COMe}$ (20 h). Similarly, $(\text{EtO})_3\text{SiH}$ or $\text{Me}(\text{EtO})_2\text{SiH}$ activated by CsF allows the quantitative and 100%

carbon double bond, or a bromo, nitro, amido, or ester group. In these cases only the aldehyde or ketone is reduced. Reactions were carried out under nitrogen by adding a mixture of the carbonyl compounds and the silane to the anhydrous salt. The reductions were followed by i.r., ^1H n.m.r. spectroscopy, and g.l.c. After hydrolysis with 2 M MeONa or 1 M HCl-acetone, the products were isolated and identified.

TABLE. Selective reduction of organic functional groups.

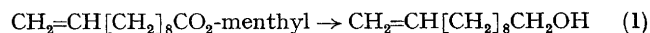
Substrate	Silane ^a	Salt ^b	T/°C	Time	Isolated compound	% Yield
$\text{PhCH}=\text{CHCHO}$	$(\text{EtO})_3\text{SiH}$	KF	25	24 h	$\text{PhCH}=\text{CHCH}_2\text{OH}$	95
$\text{Me}_2\text{C}=\text{CH}[\text{CH}_2]_2\text{CH}(\text{Me})\text{CH}_2\text{CHO}$	$(\text{EtO})_3\text{SiH}$	KF	25	1 h	$\text{Me}_2\text{C}=\text{CH}[\text{CH}_2]_2\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{OH}$	80
$p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$	$(\text{EtO})_3\text{SiH}$	KF	100	2 h	$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	80
PhCOCHBrMe	$(\text{EtO})_3\text{SiH}$	CsF	25	30 min	PhCHOHCHBrMe	70
3-Bromocamphor	$(\text{EtO})_3\text{SiH}$	CsF	70	3 h	3-Bromoborneol	60
$\text{PhCO}[\text{CH}_2]_2\text{CO}_2\text{Me}$	$\text{Me}(\text{EtO})_2\text{SiH}$	CsF	25	2.5 h	4-Phenylbutyrolactone	85
$\text{Pr}^t\text{O}_2\text{C}[\text{CH}_2]_2\text{COCO}_2\text{Pr}^t$	$(\text{EtO})_3\text{SiH}$	CsF	0	30 min	$\text{Pr}^t\text{O}_2\text{C}[\text{CH}_2]_2\text{CHOHCO}_2\text{Pr}^t$	70
$p\text{-MeCONHC}_6\text{H}_4\text{CHO}$	$(\text{EtO})_3\text{SiH}$	CsF	80	8 h	$p\text{-MeCONHC}_6\text{H}_4\text{CH}_2\text{OH}$	80
$\text{MeCOCH}_2\text{CONHPh}$	$(\text{EtO})_3\text{SiH}$	CsF	25	10 h	$\text{MeCHOHCH}_2\text{CONHPh}$	90
$\text{H}_2\text{C}=\text{CH}[\text{CH}_2]_2\text{COMe}$	$(\text{EtO})_3\text{SiH}$	CsF	0	15 min	$\text{H}_2\text{C}=\text{CH}[\text{CH}_2]_2\text{CHOHMe}$	90

^a A slight excess of silane with respect to substrate was used. ^b 1 mol. equiv. of salt with respect to substrate.

selective reduction of ketones in the following equimolar mixtures of ketones and esters:† $\text{PhCOMe} + \text{PhCO}_2\text{Et}$ [$(\text{EtO})_3\text{SiH}$; 1 min]; $\text{PhCH}_2\text{COMe} + \text{Me}[\text{CH}_2]_{10}\text{CO}_2\text{Et}$ [$\text{Me}(\text{EtO})_2\text{SiH}$; 5 h]; cyclohexanone + PhCO_2Et [$(\text{EtO})_3\text{SiH}$; 1 min].

The high selectivity of our system compared to others¹ is shown particularly clearly with bifunctional compounds (Table). We studied the reduction of aldehydes and ketones having another functional group such as a carbon-

This system is very selective and convenient: the silanes are easily available and the salts can be reused. It is also of wide application, as illustrated by the selective reduction of the ester group of menthyl undec-10-enoate [reaction (1); $\text{HSi}(\text{OEt})_3$, CsF; 60 °C; 9 h; 75% yield].



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† Conditions: 1:1 mol. equiv. of silane with respect to aldehyde or ketone; 1 mol. equiv. of KF or CsF; 25 °C; extent of reduction and identity of products determined by g.l.c. and ^1H n.m.r. spectroscopy.

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