Selective Reduction of Carbonyl Compounds by Heterogeneous Catalysis on Salt Surfaces

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Summary $(EtO)_3SiH$ and $Me(EtO)_2SiH$ 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. $(EtO)_3SiH$ and $Me(EtO)_2SiH$, 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. $(EtO)_3SiH$ activated by KF reduces aldehydes quantitatively with 100% selectivity in the following equimolar mixtures of aldehydes and ketones:† PhCHO + PhCOMe (36 h reaction time); $Me[CH_2]_5CHO$ + $PhCH_2COCH_2Ph$ (7 h); PhCHO + Bu^tCOMe (20 h). Similarly, $(EtO)_3SiH$ or $Me(EtO)_2SiH$ activated by CsF allows the quantitative and 100% selective reduction of ketones in the following equimolar mixtures of ketones and esters:† PhCOMe + $PhCO_2Et$ [$(EtO)_3SiH$; 1 min]; $PhCH_2COMe$ + $Me[CH_2]_{10}CO_2Et$ [$Me(EtO)_2SiH$; 5 h]; cyclohexanone + $PhCO_2Et$ [$(EtO)_3SiH$; 1 min].

The high selectivity of our system compared to others[1] is shown particularly clearly with bifunctional compounds (Table). We studied the reduction of aldehydes and ketones having another functional group such as a carbon–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
PhCH=CHCHO	$(EtO)_3SiH$	KF	25	24 h	$PhCH=CHCH_2OH$	95
$Me_2C=CH[CH_2]_2CH(Me)CH_2CHO$	$(EtO)_3SiH$	KF	25	1 h	$Me_2C=CH[CH_2]_2CH(Me)CH_2CH_2OH$	80
p-$NO_2C_6H_4CHO$	$(EtO)_3SiH$	KF	100	2 h	p-$NO_2C_6H_4CH_2OH$	80
PhCOCHBrMe	$(EtO)_3SiH$	CsF	25	30 min	PhCHOHCHBrMe	70
3-Bromocamphor	$(EtO)_3SiH$	CsF	70	3 h	3-Bromoborneol	60
$PhCO[CH_2]_2CO_2Me$	$Me(EtO)_2SiH$	CsF	25	2·5 h	4-Phenylbutyrolactone	85
$Pr^iO_2C[CH_2]_2COCO_2Pr^i$	$(EtO)_3SiH$	CsF	0	30 min	$Pr^iO_2C[CH_2]_2CHOHCO_2Pr^i$	70
p-$MeCONHC_6H_4CHO$	$(EtO)_3SiH$	CsF	80	8 h	p-$MeCONHC_6H_4CH_2OH$	80
$MeCOCH_2CONHPh$	$(EtO)_3SiH$	CsF	25	10 h	$MeCHOHCH_2CONHPh$	90
$H_2C=CH[CH_2]_2COMe$	$(EtO)_3SiH$	CsF	0	15 min	$H_2C=CH[CH_2]_2CHOHMe$	90

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

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); $HSi(OEt_3)$, CsF; 60 °C; 9 h; 75% yield].

$$CH_2=CH[CH_2]_8CO_2\text{-menthyl} \rightarrow CH_2=CH[CH_2]_8CH_2OH \qquad (1)$$

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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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