# 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].

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

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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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