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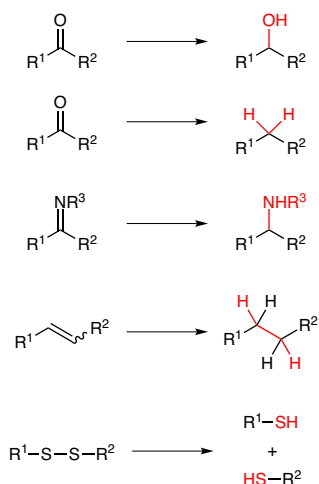
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Reducing Agents

Reduction is a chemical reaction in which the target substances receive electrons, and is one of the most fundamental reactions in organic chemistry. Reduction reactions include the deoxygenation reaction and the hydrogenation reaction. Well-known reducing agents include metal hydrides¹⁾ such as lithium aluminum hydride (= LiAlH₄) [L0203], boranes for hydride reduction, and hydrazine [H0172] used in the Wolff-Kishner reduction. A disconnection reaction of a disulfide moiety into two thiols is also considered a reduction.



This brochure introduces a variety of reducing agents and catalysts for reduction. We hope that this brochure will be useful for your research in organic synthesis. Catalysts for hydrogenation are introduced in another brochure, "Hydrogenation Catalysts".

Caution: Many reducing agents may spontaneously ignite on contact with air, or may react violently with water to produce flammable gases. Sufficient safety measures, such as using safety shields, wearing protective equipment, and using extreme caution should be taken when working with these reagents as well as in their disposal.

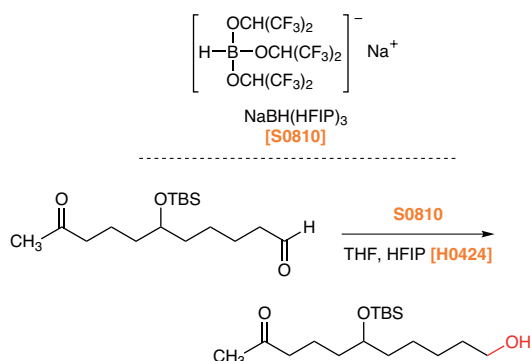
Reduction of Carbonyl Groups and Imino Group

The table below shows the reactivities of each reducing agent toward carbonyl compounds and imines. Please make use of this table as a standard for reactions.

Reactions	Imine $\text{R}-\text{C}(\text{H})=\text{NR}$	Aldehyde $\text{R}-\text{CHO}$	Ketone $\text{R}-\text{C}(=\text{O})-\text{R}$	Ester $\text{R}-\text{C}(=\text{O})-\text{OR}$	Amide $\text{R}-\text{C}(=\text{O})-\text{NR}_2$	Carboxylic Acid $\text{R}-\text{C}(=\text{O})-\text{OH}$
Reagents	Amine $\text{R}-\text{CH}_2-\text{NR}$	Alcohol $\text{R}-\text{CH}_2-\text{OH}$	Alcohol $\text{R}-\text{CH}_2-\text{OH}$	Alcohol $\text{R}-\text{CH}_2-\text{OH}$	Amine $\text{R}-\text{CH}_2-\text{NR}_2$	Alcohol $\text{R}-\text{CH}_2-\text{OH}$
NaBH₃CN [S0396]	High	Middle	Middle	Low	Low	Low
NaBH(OAc)₃ [S0394]	High	Middle	Middle	Low	Low	Low
NaBH₄ [S0480]	High	High	High	Middle	Low	Low
LiBH₄ [L0186]	High	High	High	High	Low	Low
LiAlH₄ [L0170]	High	High	High	High	Middle	Low
THF • BH₃ [T2346]	High	Middle	Middle	Low	High	High
Me₂S • BH₃ [D1843]	High	Middle	Middle	Low	High	High
PhNEt₂ • BH₃ [D2581]	High	Middle	Middle	Low	High	High

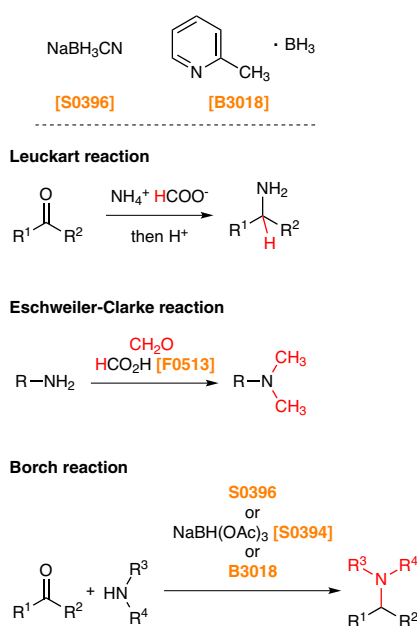
Reactivity : High Middle Low

Sodium tris(1,1,1,3,3,3-hexafluoroisopropoxy)borohydride (= NaBH(HFIP)₃) [S0810] is a selective reducing agent developed by Toshima *et al.* Aldehydes are selectively reduced in the presence of ketones and other reducible functions using S0810 to afford the corresponding primary alcohols in high yields.²⁾



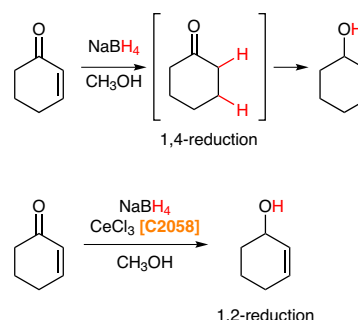
Reductive Amination

Reductive amination is a synthetic method that converts aldehydes and ketones into an amino group with an amine and a reducing agent. First, carbonyl groups and an amine form imines or iminium salts and subsequent nucleophilic attack by a reducing agent gives the amine moiety. The Leuckart reaction³⁾ and Eschweiler-Clarke reaction⁴⁾ are known as classical methods and formic acid [F0513] is used as a reducing agent in these reactions. Recently, sodium cyanoborohydride [S0396] has been frequently used for reductive amination, in what is called the Borch reaction.⁵⁾ However, this method has a problem in that S0396 has strong toxicity due to the cyano group. Meanwhile, Kikukawa *et al.* have reported a new method using 2-picoline borane [B3018].⁶⁾ B3018 is less toxic than S0396 and can be applied in both aqueous and neat conditions.



Luche Reduction

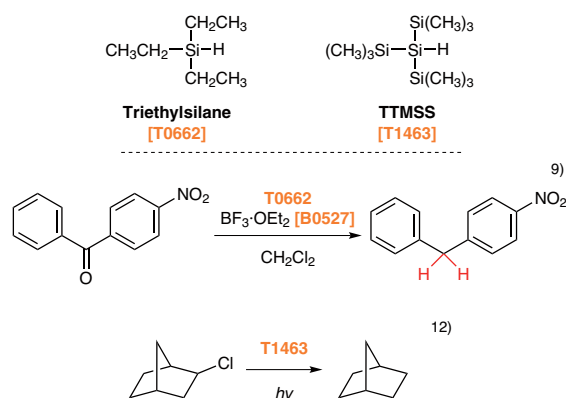
When α,β -unsaturated ketones are reduced with sodium borohydride [B0480], 1,4-reduction, not 1,2-reduction, preferentially occurs. However, Luche *et al.* have found that 1,2-reduction preferentially occurred by adding cerium(III) chloride [C2058].⁷⁾ The difference in reactivity can be explained with HSAB theory. A “hard” nucleophile is required for 1,2-reduction, whereas a hydride of S0480 is originally regarded as a “soft” nucleophile, resulting in 1,4-reduction. However, it is considered that the nucleophile turns “hard” in the presence of C2058 and alcohol. In addition, since the cerium cation works as a Lewis acid, which promotes the electrophilicity of the carbonyl group, the 1,2-addition preferentially occurs. Incidentally, an aldehyde is not reduced under this method because it forms an acetal, which is inert under these conditions.



Silane Reduction

Hydrosilanes are utilized in reduction as a hydride or a hydrogen radical source since the hydrogen atom has lower electronegativity than silicon. For instance, triethylsilane [T0662] is known as a reducing agent in the presence of a metal catalyst⁸⁾ and Lewis acid⁹⁾ and can reduce carbonyl groups and hydroxy groups into methylene moieties. T0662 is also used in the dehalogenation¹⁰⁾ reaction and in the reduction of olefins.¹¹⁾

Tris(trimethylsilyl)silane (= TTMSS) [T1463] is mainly used as a hydrogen radical source in the dehalogenation reaction.¹²⁾ In this manner, hydrosilanes and tin hydrides are currently used complementarily.



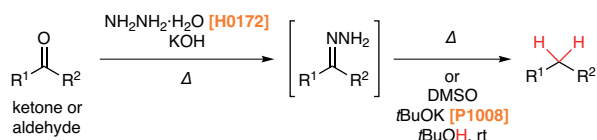
Wolff-Kishner Reduction and Clemensen Reduction

Both Wolff-Kishner reduction¹³⁾ and Clemensen reduction¹⁴⁾ are known as reactions to convert carbonyl groups into methylene groups. The Wolff-Kishner reduction can reduce carbonyl groups to methylene moieties in the presence of hydrazine [H0172], strong base, and alcohol. This reaction conventionally requires strong base and intense heat conditions, but an improved method to use a Lewis acid catalyst and a silylhydrazine derivative (Myers modification) has been developed,¹⁵⁾ which proceeds at room temperature.

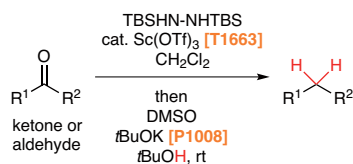
The Clemensen reduction is operated by the treatment of zinc under acidic conditions. Zinc amalgam had been used at first, but a non-aqueous modification using zinc powder and hydrogen chloride in organic solvent has been developed¹⁶⁾ and is utilized widely since mercury in amalgam is highly harmful.

The Wolff-Kishner reduction and Clemensen reduction are operated under basic and acidic conditions, respectively, so the two reactions can be used complementarily.

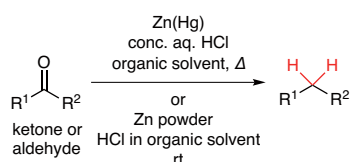
Wolff-Kishner reduction



Myers modification

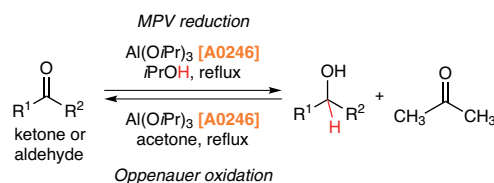


Clemensen reduction

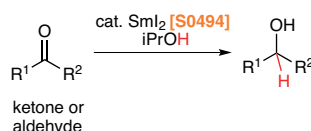


Meerwein-Ponndorf-Verley Reduction

In the Meerwein-Ponndorf-Verley (MPV) reduction, ketones and aldehydes can be reduced to alcohols by the treatment of aluminum isopropoxide [A0246] in isopropyl alcohol [I0163] solvent with heat.¹⁷⁾ This reaction is an equilibrium reaction, so an excess amount of A0246 is needed to bias the reaction toward the desired alcohol. This reaction has an advantage in that it does not affect other functional groups. Following the first report, a modified method using a catalytic amount of samarium(II) iodide¹⁸⁾ [S0494] instead of an excess amount of A0246 and asymmetric MPV reactions¹⁹⁾ was reported. Incidentally, the Oppenauer oxidation²⁰⁾ is regarded as an opposite reaction of MPV reduction and it proceeds under acetone solvent to oxidize alcohols to carbonyl groups.

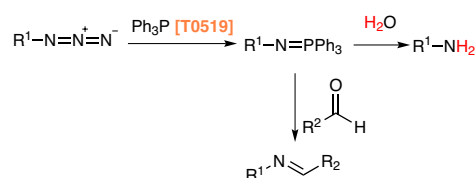


Sml₂-catalyzed MPV reduction



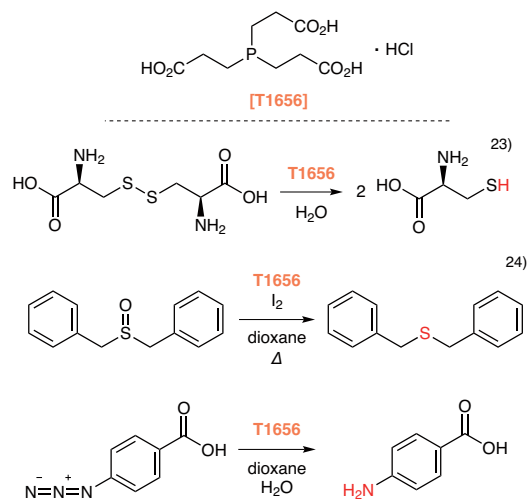
Staudinger Reaction

The Staudinger reaction is utilized to convert an azide to an amine²¹⁾ and can be regarded as a reduction in the sense of the addition of a hydrogen atom. When an azide is treated with triphenylphosphine [T0519], an iminophosphorane is formed with the elimination of a nitrogen molecule. The iminophosphorane is hydrolyzed to give the amine moiety. In contrast, the iminophosphorane gives an imine via the aza-Wittig reaction when treated with aldehydes or ketones.²²⁾



● Reducing Agent to Disconnect Disulfide Bond

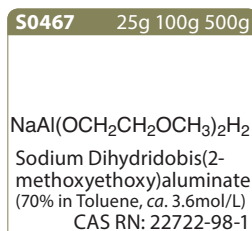
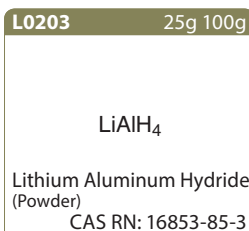
Tris(2-carboxyethyl)phosphine hydrochloride [T1656] can reduce a disulfide bond to give two thiols.²³⁾ In addition, T1656 can remove the oxygen atom on *N*-oxides and sulfoxides and can be applied to the Staudinger reaction.²⁴⁾ In this manner, T1656 shows interesting effects in the reductions of heteroatoms.



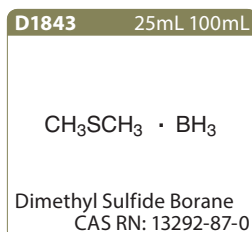
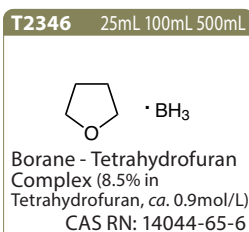
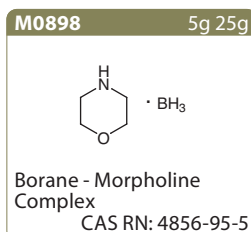
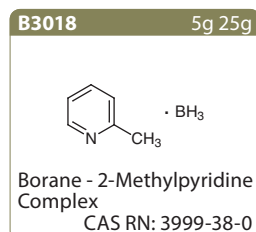
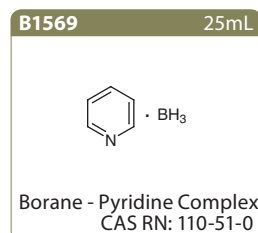
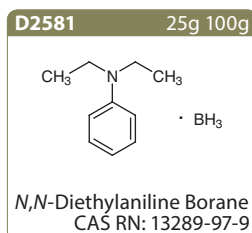
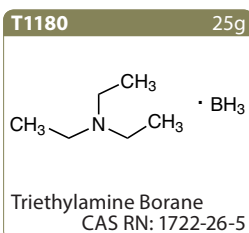
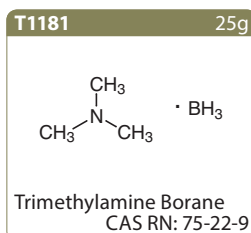
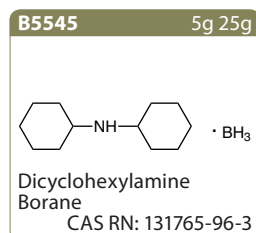
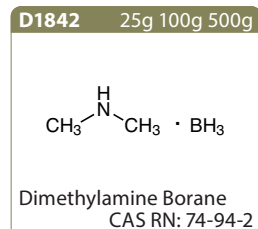
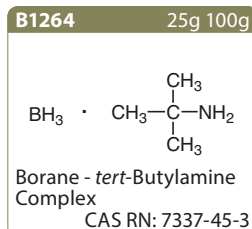
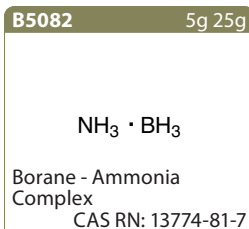
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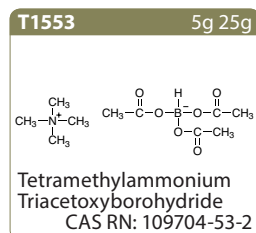
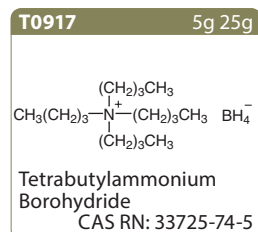
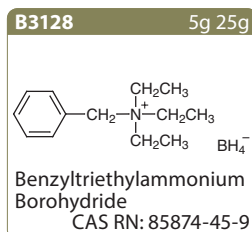
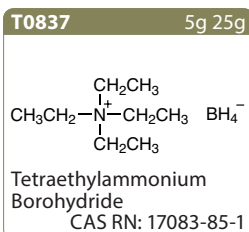
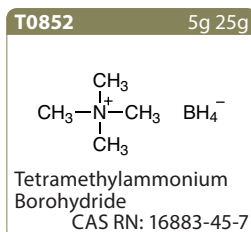
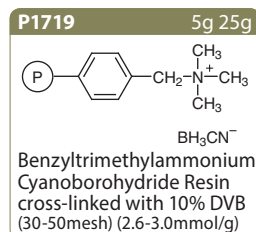
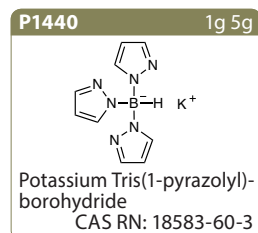
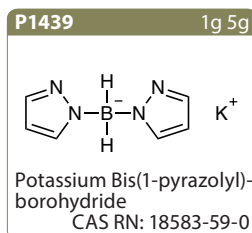
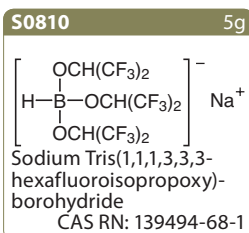
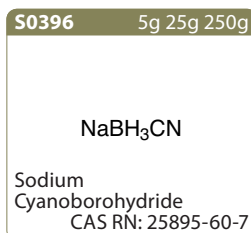
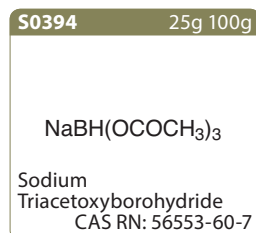
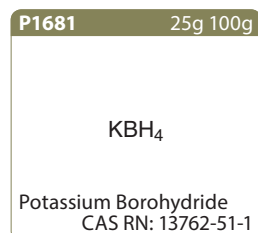
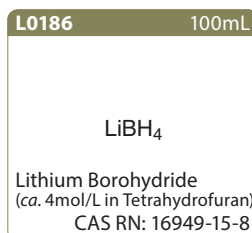
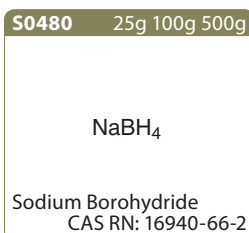
Aluminum Hydrides



Boranes



Borohydrides



Metal Hydrides

S0481 100g 500g



Sodium Hydride (60%,
dispersion in Paraffin Liquid)
CAS RN: 7646-69-7

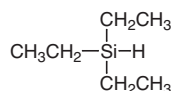
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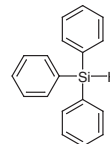
Silanes

T0662 25mL 250mL



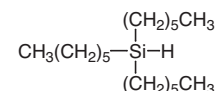
Triethylsilane
CAS RN: 617-86-7

T0661 5g 25g



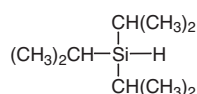
Triphenylsilane
CAS RN: 789-25-3

T1334 10g



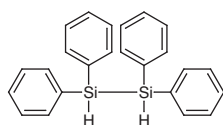
Trihexylsilane
CAS RN: 2929-52-4

T1533 5mL 25mL 100mL



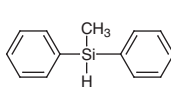
Triisopropylsilane
CAS RN: 6485-79-6

T1896 1g 5g



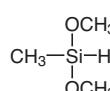
1,1,2,2-Tetraphenyldisilane
CAS RN: 16343-18-3

D1825 25mL



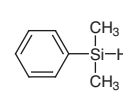
Methylphenyldiphenylsilane
CAS RN: 776-76-1

D2100 25mL 100mL



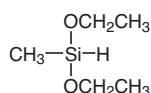
Dimethoxy(methyl)silane
CAS RN: 16881-77-9

D2196 5mL 25mL



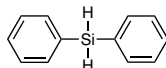
Dimethylphenylsilane
CAS RN: 766-77-8

D2403 25mL



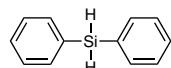
Diethoxymethylsilane
CAS RN: 2031-62-1

D2406 5g 25g



Diphenylsilane (>97.0%)
CAS RN: 775-12-2

D2820 5g 25g



Diphenylsilane (>98.0%)
CAS RN: 775-12-2

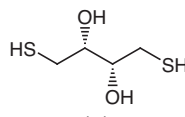
P1291 5mL 25mL



Phenylsilane
CAS RN: 694-53-1

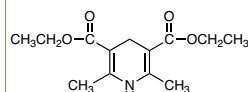
Other Reduction Reagents

D1071 1g 5g 25g



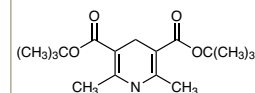
relative
DL-Dithiothreitol
CAS RN: 3483-12-3

D3775 1g 5g 25g



Hantzsch Ester
CAS RN: 1149-23-1

D4311 1g 5g



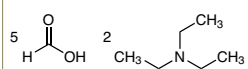
Di-tert-butyl 1,4-Dihydro-
2,6-dimethyl-3,5-
pyridinedicarboxylate
CAS RN: 55536-71-5

D5792 5g 25g 100g



SD Super Fine™ (Sodium
25wt% dispersion in mineral oil)
CAS RN: 7440-23-5

F1202 25mL 100mL



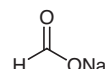
TEAF
CAS RN: 15077-13-1

F0513 300mL



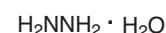
Formic Acid
CAS RN: 64-18-6

S0807 500g



Sodium Formate
CAS RN: 141-53-7

H0172 25mL 500mL



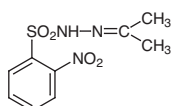
Hydrazine Monohydrate
CAS RN: 7803-57-8

H1221 300mL



Hydriodic Acid (57%)
CAS RN: 10034-85-2

I0777 1g 5g



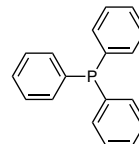
IPNBSH
CAS RN: 6655-27-2

S0494 25mL 100mL



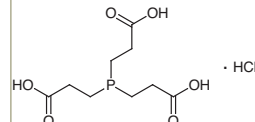
Samarium(II) Iodide (ca.
0.1mol/L in Tetrahydrofuran)
CAS RN: 32248-43-4

T0519 25g 100g 500g



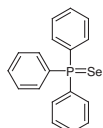
Triphenylphosphine
CAS RN: 603-35-0

T1656 1g 5g 25g



Tris(2-carboxyethyl)-
phosphine Hydrochloride
CAS RN: 51805-45-9

T1819 5g



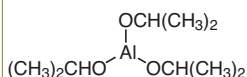
Triphenylphosphine
Selenide
CAS RN: 3878-44-2

C2058 5g 25g



Cerium(III) Chloride
Anhydrous
CAS RN: 7790-86-5

A0246 100g 500g



Aluminum Isopropoxide
CAS RN: 555-31-7

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