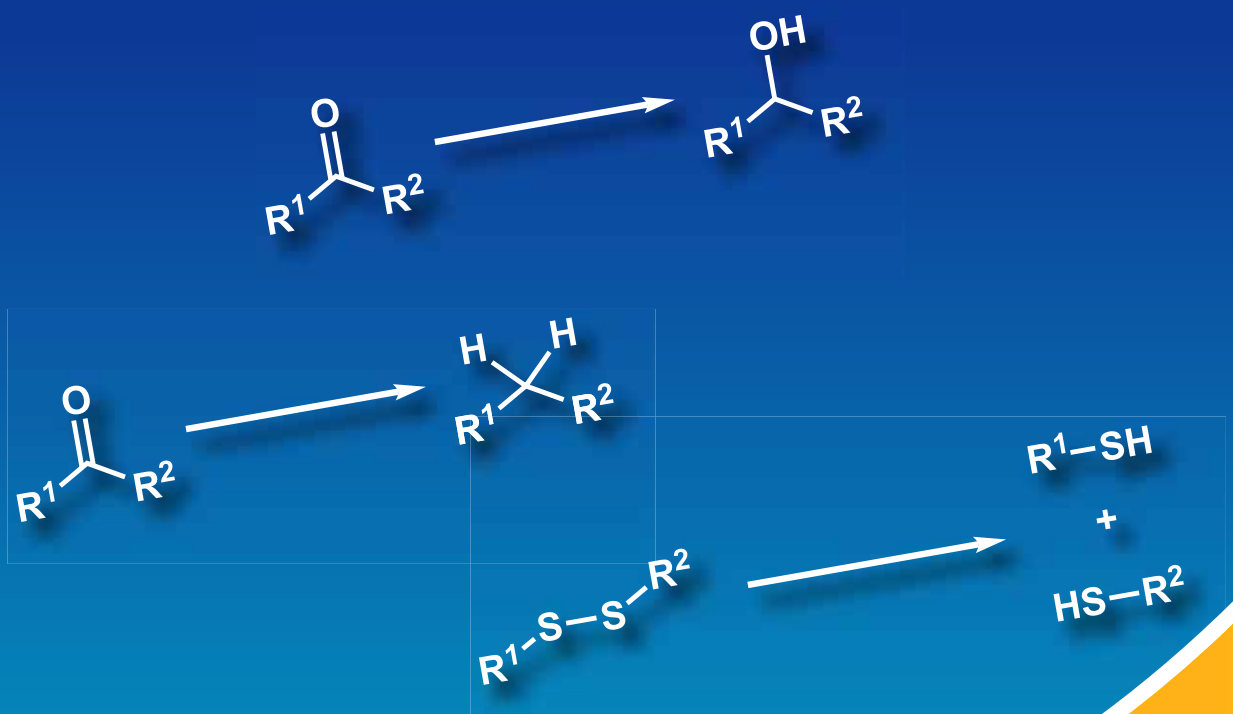
CHEMISTRY

还原剂
Reducing Agents



氢化铝

硼烷

硼氢化物

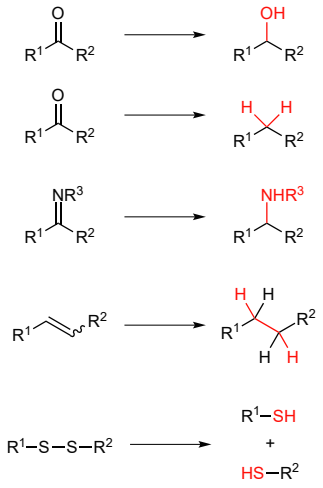
金属氢化物

硅烷

其它还原剂

还原剂

还原反应是目标物质接受电子的化学反应，是有机化学最基础的反应之一。还原反应包括去氧化反应和氢化反应。著名的还原试剂包括金属氢化物[1)]如氢化铝锂(= $LiAlH_4$) [L0203]，用于氢化还原反应的硼烷试剂和用于Wolff-Kishner反应的肼试剂[H0172]。双硫部分的裂解反应为二硫醇也可以视为还原反应。



手册介绍了大量用于还原反应的还原试剂和催化剂。我们希望该手册对于您的有机合成研究有所帮助。氢化反应催化剂在另外的手册氢化催化剂中也有介绍。

注意：许多还原试剂在接触空气后可自燃，或者与水剧烈反应生成可燃性气体。在处理这些试剂以及废弃的过程中需要配备充足的防护用具，穿戴防护装备以及需要极度小心。

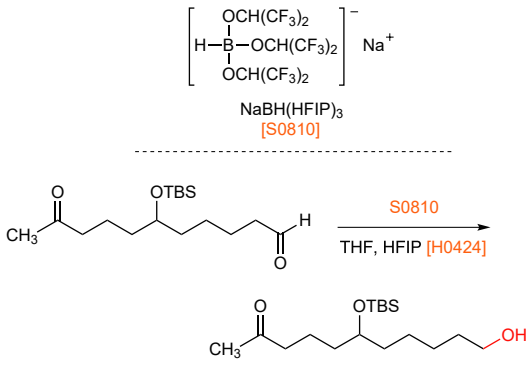
● 羰基和亚胺基的还原反应

下面这张表格显示了每个还原试剂对羰基和亚胺基的反应活性，请使用这个表格作为反应的标准。

Reagents \ Reactions	Imine → Amine	Aldehyde → Alcohol	Ketone → Alcohol	Ester → Alcohol	Amide → Amine	Carboxylic Acid → Alcohol
$NaBH_3CN$ [S0396]	High	Middle	Middle	Low	Low	Low
$NaBH(OAc)_3$ [S0394]	High	Middle	Middle	Low	Low	Low
$LiBH_4$ [L0186]	High	High	High	High	Low	Low
$LiAlH_4$ [L0170]	High	High	High	High	Middle	Low
$THF \cdot BH_3$ [T2346]	High	Middle	Middle	Low	High	High
$Me_2S \cdot BH_3$ [D1843]	High	Middle	Middle	Low	High	High
$PhNEt_2 \cdot BH_3$ [D2581]	High	Middle	Middle	Low	High	High

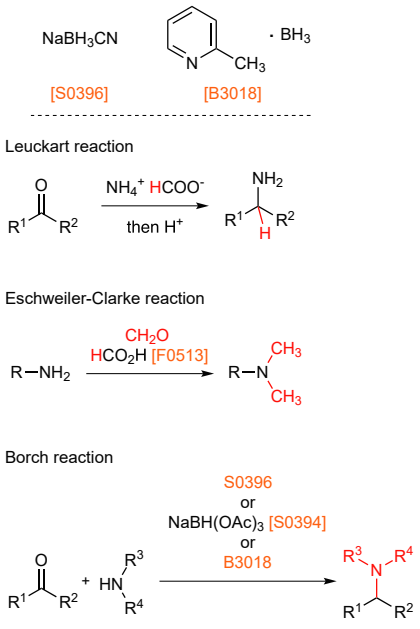
Reactivity : High | Middle | Low

三(1,1,1,3,3,3-六氟异丙氧基)硼氢化钠(=$NaBH(HFIP)_3$) [S0810]是由Toshima等研发的选择性还原试剂。使用S0810时，在酮和其他可还原性基团存在下可以选择性将醛以高产率还原为相应的伯醇[2]。



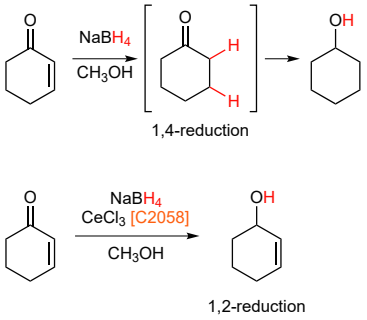
● 还原氨化反应

还原氨化可以将醛或酮转变为含胺基的氨基和还原剂。首先，羰基和氨基形成亚胺或亚胺盐，经过后续还原剂的亲核进攻形成氨基。Leuckart反应[3]和Eschweiler-Clarke反应[4]是经典的合成方法，甲酸[F0513]在这些反应中用作还原剂。近期，氰基硼氢化钠[S0396]常用于还原氨化反应，称为Borch反应[5]。但是，这种方法的问题在于S0396由于含有氰基而具有强毒性。与此同时，Kikukawa等报道了使用2-甲基吡啶硼烷[B3018]的新方法[6]。B3018毒性小于S0396，可以应用于水相和无溶剂条件。



● Luche还原反应

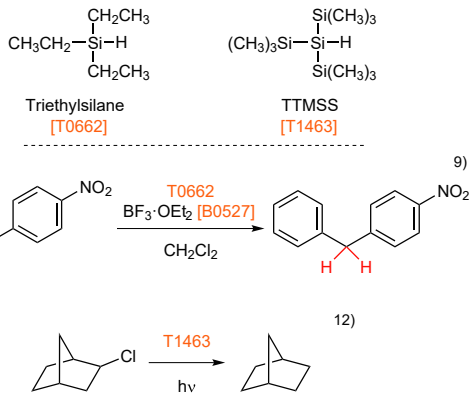
当 α,β-不饱和酮使用硼氢化钠还原时, 可以优先发生1,4-还原，而非1,2-还原。但是，Luche等发现添加氯化铈(III)[C2058][7]情况下1,2-还原优先发生。反应性的差异可以用HSAB理论来解释。1,2-还原需要“硬”亲核剂，而硼氢化钠的氢化物最初被视为“软”亲核剂，可以发生1,4-还原。然而，有人认为，在C2058和乙醇的存在下，亲核分子会变“硬”。此外，由于铈阳离子起到Lewis酸的作用，促进了羰基的亲电性，所以1,2-加成优先发生。另外，在这种方法下醛不会被还原，因为形成了一种缩醛，在这些条件下具有惰性。



● 硅烷还原反应

羟基硅烷可以用于还原反应中的氢化物或氢自由基源，因为氢原子与硅相比较具有低的电负性。例如：triethylsilane[T0662]在金属催化剂[8]和Lewis酸[9]存在下可以将羰基和羟基转变为亚甲基。T0662可以用于脱卤反应[10]和烯烃还原[11]。

三(三甲硅基)硅烷（=TTMSS）在脱卤反应中主要用于氢自由基源[12]。在这种方式下，羟硅基和锡化氢可以互补使用。

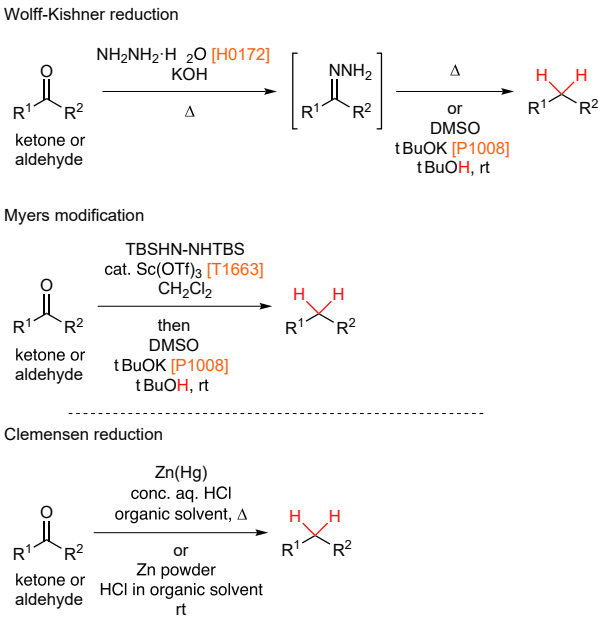


● Wolff-Kishner还原反应

Wolff-Kishner还原反应[13]和Clemensen还原反应[14]可以将羰基转变为亚甲基。Wolff-Kishner还原反应在肼、强碱和醇条件下可以将羰基转变为亚甲基。传统条件下，反应需要强碱和高热条件。这个改善的方法可以使用Lewis酸催化剂和硅基肼衍生物（Myers修饰）[15]，该反应室温下可以进行。

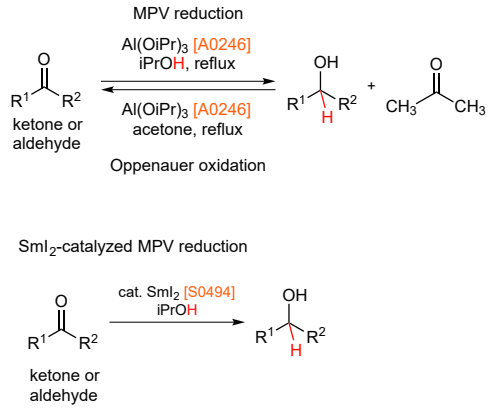
Clemensen还原需要锌在酸性条件下操作。最初使用锌汞齐，但由于汞齐中汞的危害性很大，后来在有机溶剂中采用锌粉和氯化氢进行非水性改性，并得到了广泛使用[16]。

Wolff-Kishner还原反应和Clemensen还原反应分别在碱性和酸性条件下操作，所以这两种反应可以互补使用。



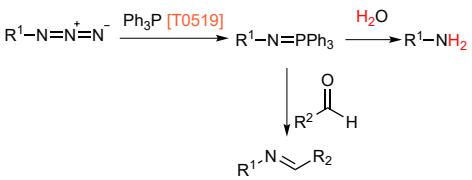
● Meerwein-Ponndolf-Verley还原反应

在Meerwein-Ponndolf-Verley(MPV)还原反应中，酮和醛在加热条件下用溶剂异丙醇[I0163]中的异丙氧基铝[A0246]处理可以还原得到醇[17]。这是一个平衡反应，所以需要过量的A0246来使反应偏向所需的醇。这个反应具有的优势是它不影响其他官能团。在此报道之后，又报道了改进方法是使用催化量的碘化钐(II)[18][S0494]，而不是过量的A0246和不对称MPV反应[19]的报道。偶尔情况下，Oppenauer氧化反应[20]是MPV反应的逆反应，反应在丙酮为溶剂条件下可以将醇氧化为羰基。



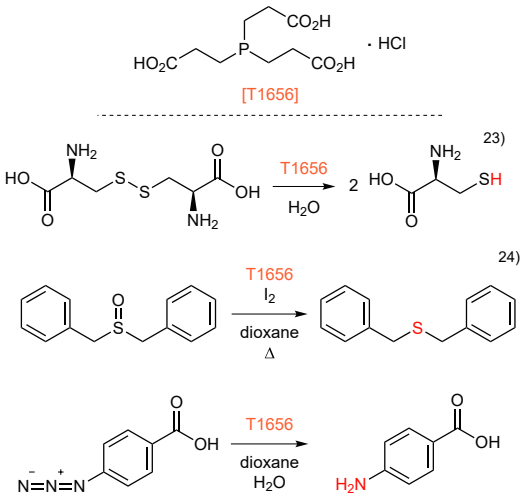
● Staudinger反应

Staudinger反应可以将叠氮转化为胺[21]，从氢原子加成条件下可以视为还原反应。将叠氮化物使用三苯基膦[T0519]处理时，氮分子消除可以形成亚胺膦，亚胺膦水解生成胺。相对照条件下，亚胺膦使用醛和酮处理时经过aza-Wittig反应可以得到亚胺[22]。



● 可裂解二硫键的还原剂

三(2-羧乙基)膦盐酸盐 [T1656]可以将二硫键还原得到二硫醇[23]。此外，T1656可以除去*N*-氧化物和硫氧化物中的氧原子，可应用于Staudinger reaction[24]。在这个条件下，T1656也因此在杂原子的还原中显示出有趣的效果。



参考文献

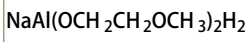
1) Review: J. Málek, M. Černý, *Synthesis* **1972**, 217.
2) Y. Kuroiwa, S. Matsumura, K. Toshima, *Synlett* **2008**, *16*, 2523.
3) R. Leuckart, *Ber.* **1885**, *18*, 2341.
4) a) W. Eschweiler, *Ber.* **1905**, *38*, 880.
   b) H. T. Clarke, H. B. Gillespie, S. Z. Weisshaus, *J. Am. Chem. Soc.* **1933**, *55*, 4571.
5) a) R. F. Borch, M. D. Bernstein, H. D. Durst, *J. Am. Chem. Soc.* **1971**, *93*, 2897.
   b) R. F. Borch, A. I. Hassid, J. *Org. Chem.* **1972**, *37*, 1673.
6) S. Sato, T. Sakamoto, E. Miyazawa, Y. Kikugawa, *Tetrahedron* **2004**, *60*, 7899.
7) a) J. L. Luche, *J. Am. Chem. Soc.* **1978**, *100*, 2226.
   b) J.-L. Luche, L. Rodriguez-Hahn, P. Crabbé, *J. Chem. Soc., Chem. Commun.* **1978**, 601.
8) M. Mirza-Aghayan, M. Kalantari, R. Boukherroub, *Appl. Organomet. Chem.* **2019**, *33*, e4837.
9) I. Smonou, *Synth. Commun.* **1994**, *24*, 1999.
10) R. P. Allen, B. P. Roberts, C. R. Willis, *J. Chem. Soc., Chem. Commun.* **1989**, 1387.
11) A. R. Jesus, A. P. Marques, A. P. Rauter, *Pure Appl. Chem.* **2016**, *88*, 349.
12) C. Chatgilialoglu, D. Griller, M. Lesage, *J. Org. Chem.* **1988**, *53*, 3641.
13) a) Kishner, *N. J. Russ. Phys. Chem. Soc.* **1911**, *43*, 582.
   b) L. Wolff, *Ann.* **1912**, *394*, 86.
14) a) E. Clemmensen, *Ber.* **1913**, *46*, 1837.
   b) E. Clemmensen, *Ber.* **1914**, *47*, 51.
   c) E. Clemmensen, *Ber.* **1914**, *47*, 681.
15) M. E. Furrow, A. G. Myers, *J. Am. Chem. Soc.* **2004**, *126*, 5436.
16) a) S. Yamamura, S. Ueda, Y. Hirata, *Chem. Commun.* **1967**, 1049.
   b) S. Yamamura, Y. Hirata, *J. Chem. Soc. C* **1968**, 2887.
   c) M. Toda, M. Hayashi, Y. Hirata, S. Yamamura, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 264.
17) a) H. Meerwein, R. Schmidt, *Ann.* **1925**, *444*, 221.
   b) A. Verley, *Bull. Soc. Chim. Fr.* **1925**, *37*, 537.
   c) W. Ponndorf, *Angew. Chem.* **1926**, *39*, 138.
18) J. L. Namy, J. Souppe, J. Collin, H. B. Kagan, *J. Org. Chem.* **1984**, *49*, 2045.
19) D. A. Evans. S. G. Nelson, M. R. Gagne, A. R. Muci, *J. Am. Chem. Soc.* **1993**, *115*, 9800.
20) R. V. Oppenauer, *Rec. Trav. Chim. Pays-Bas* **1937**, *56*, 137.
21 H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 635.
22) T. Sasaki, S. Eguchi, T. Okano, *J. Am. Chem. Soc.* **1983**, *105*, 5912.
23) J. A. Burns, J. C. Butler, J. Moran, G. M. Whitesides, *J. Org. Chem.* ***1991***, *56*, 2648.
24) A. M. Faucher, C. Grand-Maître, *Synth. Commun.* **2003**, *33*, 3503.

氢化铝
Aluminum Hydrides

L0203 25g 100g

Lithium Aluminum Hydride
(Powder)
CAS RN: 16853-85-3

S0467 25g 100g 500g



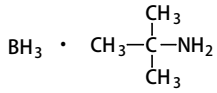
Sodium Dihydridobis(2-methoxyethoxy)aluminate
(70% in Toluene, *ca.* 3.6mol/L)
CAS RN: 22722-98-1

硼烷
Boranes

B5082 5g 25g

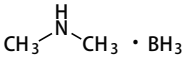
Borane - Ammonia Complex
CAS RN: 13774-81-7

B1264 25g 100g



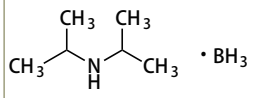
Borane - *tert*-Butylamine Complex
CAS RN: 7337-45-3

D1842 25g 100g 500g



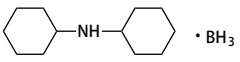
Dimethylamine Borane
CAS RN: 74-94-2

B5544 25g



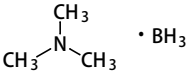
Borane - Diisopropylamine Complex
CAS RN: 55124-35-1

B5545 5g 25g



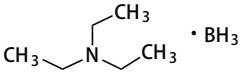
Dicyclohexylamine Borane
CAS RN: 131765-96-3

T1181 25g



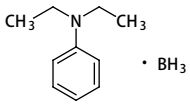
Trimethylamine Borane
CAS RN: 75-22-9

T1180 25g



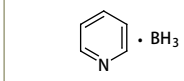
Triethylamine Borane
CAS RN: 1722-26-5

D2581 25g 100g



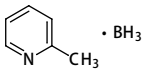
N,N-Diethylaniline Borane
CAS RN: 13289-97-9

B1569 25mL



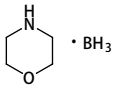
Borane - Pyridine Complex
CAS RN: 110-51-0

B3018 5g 25g



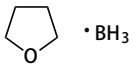
Borane - 2-Methylpyridine Complex
CAS RN: 3999-38-0

M0898 5g 25g



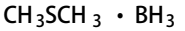
Borane - Morpholine Complex
CAS RN: 4856-95-5

T2346 100mL 500mL



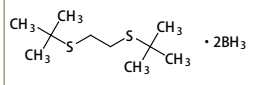
Borane - Tetrahydrofuran Complex (8.5% in Tetrahydrofuran, *ca.* 0.9mol/L)
CAS RN: 14044-65-6

D1843 25mL 100mL



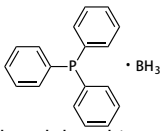
Dimethyl Sulfide Borane
CAS RN: 13292-87-0

B1827 1g



1,2-Bis(*tert*-butylthio)-ethane Borane
CAS RN: 71522-78-6

T1789 25g



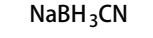
Triphenylphosphine Borane
CAS RN: 2049-55-0

硼氢化物
Borohydrides

S0394 25g 100g

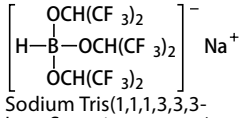
Sodium Triacetoxyborohydride
CAS RN: 56553-60-7

S0396 5g 25g 250g



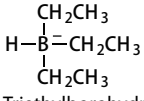
Sodium Cyanoborohydride
CAS RN: 25895-60-7

S0810 5g



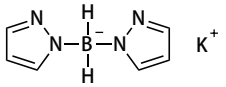
Sodium Tris(1,1,1,3,3,3-hexafluoroisopropoxy)-borohydride
CAS RN: 139494-68-1

L0190 100mL 500mL



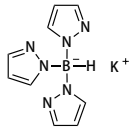
Lithium Triethylborohydride
(*ca.* 12% in Tetrahydrofuran, *ca.* 1.0mol/L)
CAS RN: 22560-16-3

P1439 1g 5g



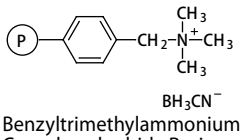
Potassium Bis(1-pyrazolyl)-borohydride
CAS RN: 18583-59-0

P1440 1g 5g



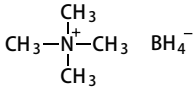
Potassium Tris(1-pyrazolyl)-borohydride
CAS RN: 18583-60-3

P1719 5g 25g



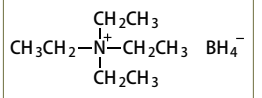
Benzyltrimethylammonium Cyanoborohydride Resin cross-linked with 10% DVB
(30-50mesh) (2.6-3.0mmol/g)

T0852 5g 25g



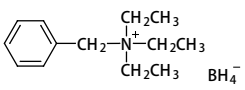
Tetramethylammonium Borohydride
CAS RN: 16883-45-7

T0837 5g 25g



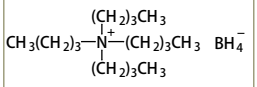
Tetraethylammonium Borohydride
CAS RN: 17083-85-1

B3128 5g 25g



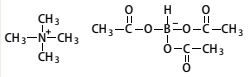
Benzyltriethylammonium Borohydride
CAS RN: 85874-45-9

T0917 5g 25g



Tetrabutylammonium Borohydride
CAS RN: 33725-74-5

T1553 5g 25g



Tetramethylammonium Triacetoxyborohydride
CAS RN: 109704-53-2

金属氢化物
Metal Hydrides

S0481 100g 500g

NaH

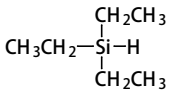
Sodium Hydride (60%, dispersion in Paraffin Liquid)
CAS RN: 7646-69-7

Z0010 1g 5g 25g

Zirconocene Chloride Hydride
CAS RN: 37342-97-5

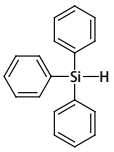
硅烷
Silanes

T0662 25mL 250mL



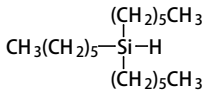
Triethylsilane
CAS RN: 617-86-7

T0661 5g 25g



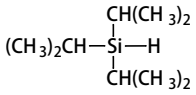
Triphenylsilane
CAS RN: 789-25-3

T1334 10g



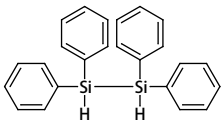
Trihexylsilane
CAS RN: 2929-52-4

T1533 5mL 25mL 100mL



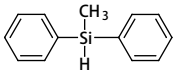
Triisopropylsilane
CAS RN: 6485-79-6

T1896 1g 5g



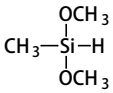
1,1,2,2-Tetraphenyldisilane
CAS RN: 16343-18-3

D1825 25mL



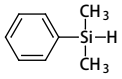
Methyldiphenylsilane
CAS RN: 776-76-1

D2100 25mL 100mL



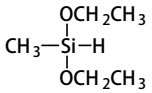
Dimethoxy(methyl)silane
CAS RN: 16881-77-9

D2196 5mL 25mL



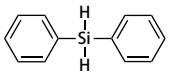
Dimethylphenylsilane
CAS RN: 766-77-8

D2403 25mL



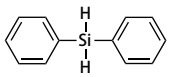
Diethoxymethylsilane
CAS RN: 2031-62-1

D2406 5g 25g



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

D2820 5g 25g



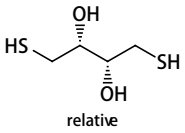
Diphenylsilane (>98.0%)
CAS RN: 775-12-2

P1291 5mL 25mL

Phenylsilane
CAS RN: 694-53-1

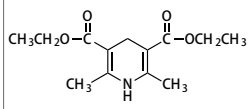
其它还原剂
Other Reduction Reagents

D1071 1g 5g 25g



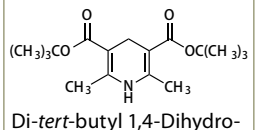
DL-Dithiothreitol
CAS RN: 3483-12-3

D3775 1g 5g 25g



Hantzsch Ester
CAS RN: 1149-23-1

D4311 1g 5g



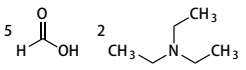
Di-*tert*-butyl 1,4-Dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate
CAS RN: 55536-71-5

C2058 5g 25g

$CeCl_3$

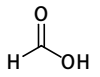
Cerium(III) Chloride Anhydrous
CAS RN: 7790-86-5

F1202 25mL 100mL



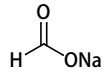
TEAF
CAS RN: 15077-13-1

F0513 300mL



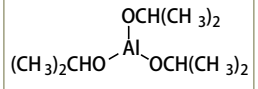
Formic Acid
CAS RN: 64-18-6

S0807 500g



Sodium Formate
CAS RN: 141-53-7

A0246 100g 500g



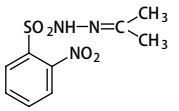
Aluminum Isopropoxide
CAS RN: 555-31-7

H1221 300mL

HI

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

I0777 1g 5g



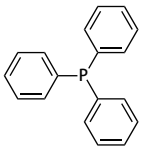
IPNBSH
CAS RN: 6655-27-2

S0494 25mL 100mL

SmI_2

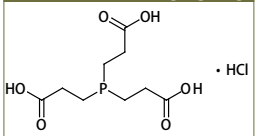
Samarium(II) Iodide (*ca.* 0.1mol/L in Tetrahydrofuran)
CAS RN: 32248-43-4

T0519 25g 100g 500g



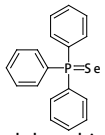
Triphenylphosphine
CAS RN: 603-35-0

T1656 1g 5g 25g



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

T1819 5g



Triphenylphosphine Selenide

CAS RN: 3878-44-2

梯希爱(上海)化成工业发展有限公司

试剂热线：800-988-0390或021-67121386

大包装热线：800-988-1865

传真：021-67121385

邮箱：Sales-CN@TCIchemicals.com

地址：上海化学工业区普工路96号

邮编： 201507

www.TCIchemicals.com

R5118C 20200327