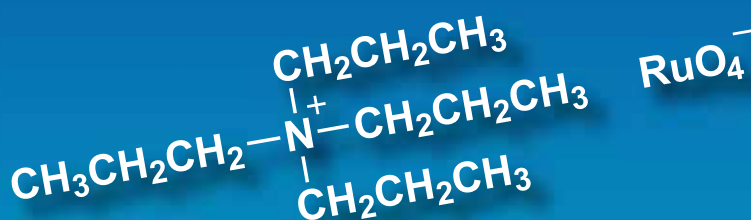
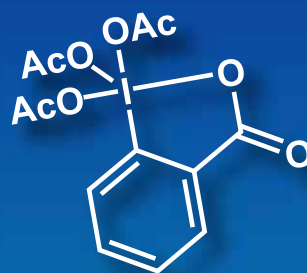
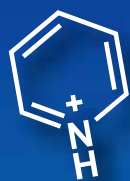


氧化剂

Oxidizing Agents



铬酸盐

次氯酸盐

高氯酸盐

过氧化物

高价碘化合物

硫氧化物

氮氧化物

其它氧化剂

氧化催化剂

氧化剂

使目标物失去电子的氧化反应是有机化学中最基础的反应之一，典型的例子就是与氧结合和脱氢反应。氧化剂经常被用于将醇转化为相应的醛、酮或羧酸。氧化铬(VI)、高锰酸钾等重金属化合物已被使用多年。后来又开发出了不含重金属的危害性较小的氧化剂，如戴斯-马丁氧化剂、Mukaiyama氧化剂、氧铵盐等。此外，还报道了用廉价的助氧化剂在四丙基高钨酸铵(TPAP)和TEMPO等氧化催化剂存在下的氧化反应。这样，涉及有机化合物的氧化反应就有了很大的多样性，已经出版了许多关于氧化的书籍¹⁾。

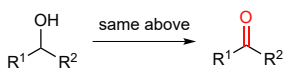
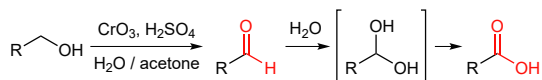
这本小册子介绍了各种氧化剂和氧化催化剂。希望对您有机合成方面的研究有所帮助。另外，我们还准备了另一本小册子《还原剂》，这是氧化的逆反应。

● 铬酸盐

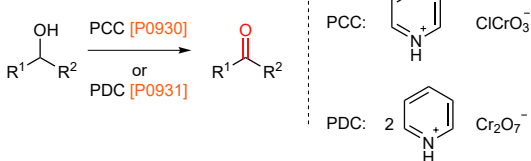
Jones等报道了氧化铬(VI)和稀硫酸的混合物可用于对醇的氧化，这种反应称为Jones氧化²⁾。它可将伯醇和仲醇分别转化为羧酸和酮。自此之后，铬氧化剂得到了改进，发展成为使用复合氧化铬(VI)-2py、氯铬酸吡啶(PCC)[P0930]⁴⁾和重铬酸吡啶(PDC)[P0931]⁵⁾的Sarett-Collins氧化³⁾工艺。这些试剂可以将伯醇氧化成醛而不发生过度反应。

注意：铬(VI)化合物和反应后的铬渣毒性高，处理或丢弃时应考虑环境因素。

Jones oxidation

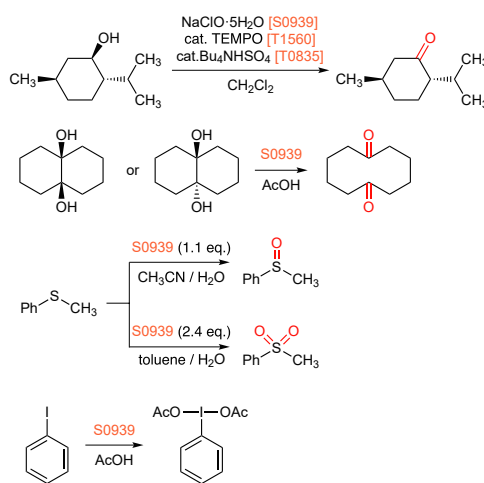


PCC and PDC oxidation



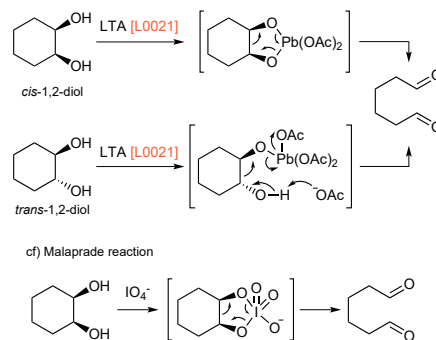
● 次氯酸钠

次氯酸钠五水合物(NaClO·5H₂O) [S0939] 是一种稳定的结晶固体，可有效氧化羟基和硫化物。例如，S0939可以在催化剂量的TEMPO[T1560]存在下将仲醇氧化成酮⁶⁾。S0939也可用于1,2-二醇⁷⁾的氧化裂解和硫化物的氧化⁸⁾。通过调整S0939的当量，可以高收率地合成亚砷和砷。此外，最近有报道称，S0939可用于高价碘化合物的简便合成⁹⁾。



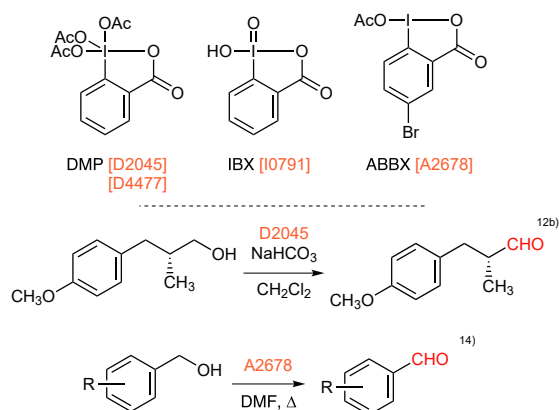
● Criegee氧化反应

Criegee氧化反应在反应中使用四乙酸铅(IV)(LTA) [L0021]氧化1,2-二醇获得两种酮或醛¹⁰⁾。这个反应不同于高碘酸盐的氧化裂解反应(=Malprade反应)¹¹⁾，并且可以和难以形成五元环中间体的反式1,2-二醇反应。由此可以推断出另一种不通过环状过渡态的反应机理。



● 使用高价碘化合物的氧化反应

戴斯-马丁氧化剂 (DMP)¹²[D2045] [D4477]可以将伯醇和仲醇分别氧化成醛和酮。与四价铬酸盐化合物相比, DMP具有一些优势: DMP在温和的条件下进行反应; 活性底物普适范围宽; 对环境的影响较低; 反应后处理简单。Togo开发的2-碘酰基苯甲酸 (IBX)¹³[I0791]和1-乙酰氧基-5-溴-1,2-苯并碘氧杂戊环-3(1*H*)-酮 (ABBX)¹⁴[A2678]像很多高价碘化合物一样, 被用作醇的氧化剂¹⁵。这些化合物的相关介绍请参考我们的单页“高价碘化合物”。



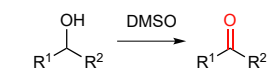
● DMSO氧化和无气味Swern氧化剂

Kornblum等发现苯基卤化物和甲苯磺酸盐可以在碱性条件下与DMSO反应生成羰基¹⁶。这篇报道后, 又出现了很多用DMSO进行氧化反应的报告: 用DCC [D0436]或DCC (粒状) [D4876]进行的Pfitzner-Moffatt氧化反应¹⁷; 用乙酸酐[A2036]进行的Albright-Goldman氧化反应¹⁸; 用吡啶-三氧化硫络合物[P0998]进行的Parikh-Doering氧化反应¹⁹以及用草酰氯[O0082]进行的Swern氧化反应²⁰。这些反应从实验室规模到工业规模都得到了广泛应用。



X = halogen, TsO

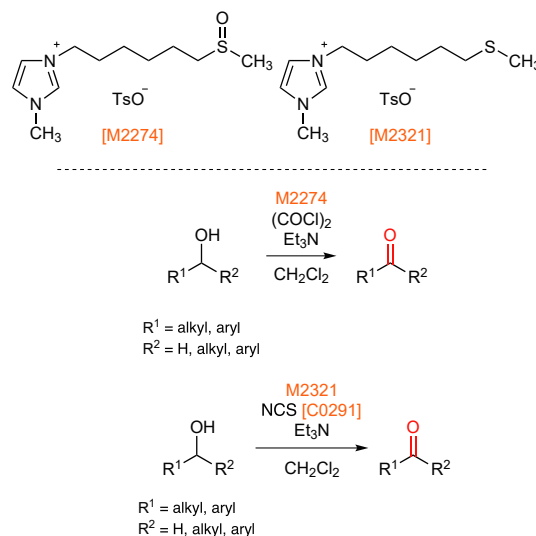
Various DMSO oxidations



R¹ = alkyl, aryl
R² = H, alkyl, aryl

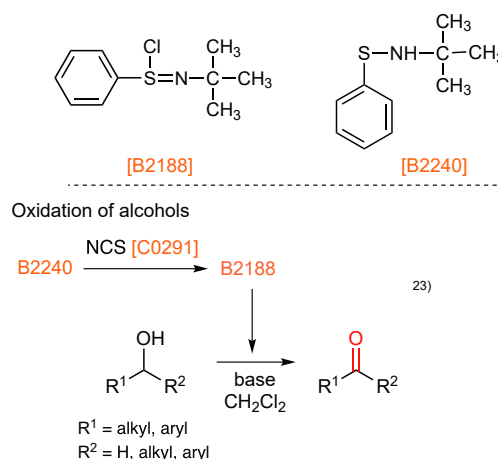
named reactions	reagents
Pfitzner-Moffatt oxid.	DCC [D0436] [D4876] TFA [T0431]
Albright-Goldman oxid.	Ac ₂ O [A2036]
Parikh-Doering oxid.	SO ₃ ·py [P0998], Et ₃ N [T0424]
Swern oxid.	(COCl) ₂ [O0082] or TFAA [T0433] Et ₃ N [T0424]

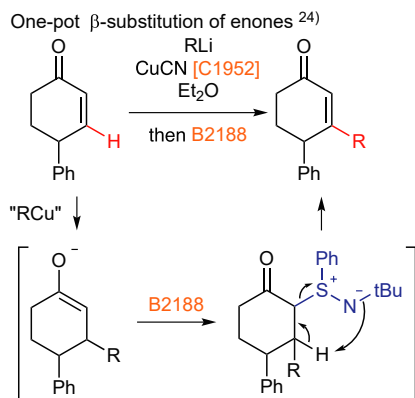
DMSO氧化的一个问题是副产品二甲基硫化物的气味。为了解决这一问题, Togo等研制了无臭可回收的咪唑盐[M2274]和[M2321], 分别用于Swern氧化^{21a)}和Corey-Kim氧化^{21b)}。



● Mukaiyama氧化反应

Mukaiyama研究组报告了两种新的氧化反应, 分别使用*N*-叔丁基苯磺亚胺酰氯[B2188]²²⁾和催化剂量的*N*-叔丁基苯亚磺酰胺[B2240]和NCS[C0291]²³⁾。一般认为B2240与NCS在位反应生成B2188, 反应后生成B2240; 因此B2240起到催化剂的作用。B2188是一种稳定的固体, 可以通过在α位上的去质子化或1,4加成从烯醇化物转化为α,β-不饱和酮²⁴⁾。此外, 据有关新方法报道, 可以通过醛、烷基锂和B2188用一锅法得到酮²⁵⁾。

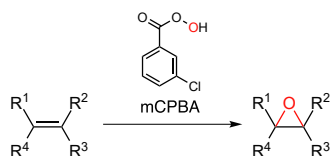




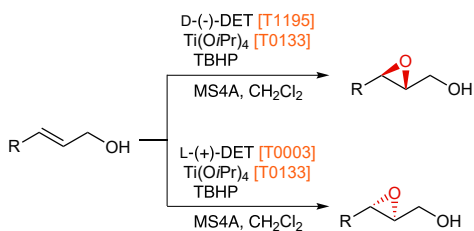
● 环氧化反应

环氧化反应也是一种氧化反应，mCPBA参与的Prilezhaev (Prileschajew)反应²⁶⁾被认为是一种典型的环氧化反应。此外，不对称环氧化反应如烯丙醇的Sharpless-Katsuki不对称环氧化反应²⁷⁾和顺式烯烃的Jacobsen-Katsuki不对称环氧化反应²⁸⁾等也有报道。Sharpless-Katsuki不对称环氧化反应经常被用于天然产物全合成。

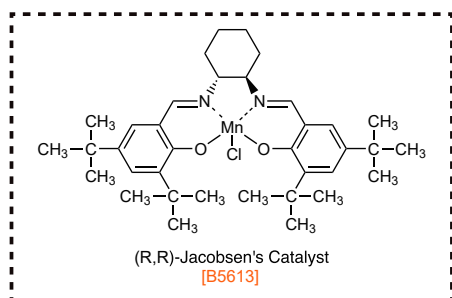
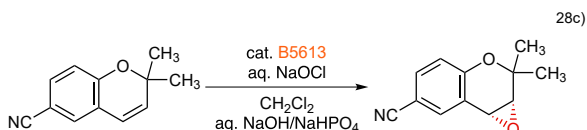
Prilezhaev epoxidation



Sharpless-Katsuki asymmetric epoxidation



Jacobsen-Katsuki asymmetric epoxidation

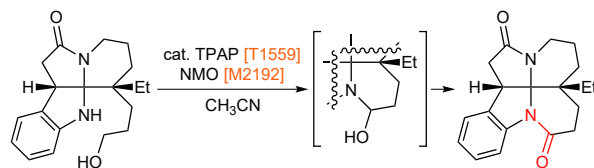
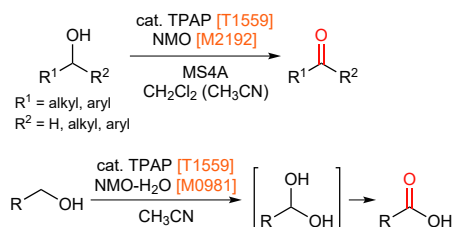


● 催化氧化反应

1. TPAP催化的氧化反应

四丙基过钨酸铵 (TPAP) [T1559] 催化剂通过添加4-甲基吗啉N-氧化物 (=NMO) [M2192] 作为助氧化剂可以把醇氧化为醛和酮 (Ley-Griffith氧化反应)²⁹⁾。该反应也可在非常温和的条件下进行，即使应用于不稳定物质，也能高收率得到相应产物。此外，该反应能在水存在下通过乙醛水化形成偕二醇并进行后续氧化，将伯醇氧化为羧酸³⁰⁾。TPAP和NMO经常被用于天然产物全合成。例如Gaich研究组就曾报道过通过在最后一步中对此反应的巧妙运用实现(-)-leuconoxine的全合成³¹⁾。

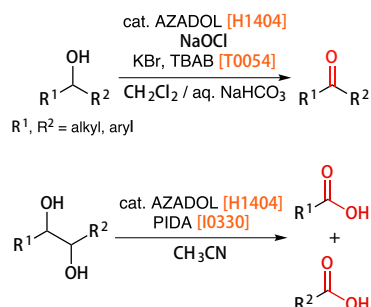
Ley-Griffith oxidation



2. AZADOL® 氧化反应

AZADOL® [H1404] 由Iwabuchi等开发的一种羟胺³²⁾，是氧化反应催化剂前体。H1404的氧化性能比TEMPO [T1560] 更具优势，特别是对仲醇。此外，1,2-二醇通过催化量的PIDA [I0330] 处理可氧化裂解生成两种羧酸。由于次氯酸钠、氯酸钠甚至空气中的氧气都可以用作其助氧化剂，H1404有望成为一种绿色的氧化催化剂。

AZADOL® 是日产化学制品公司的注册商标。



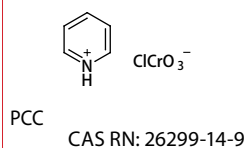
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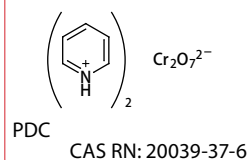
铬酸盐

Chromates

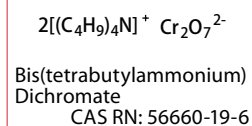
P0930 25g 100g 500g



P0931 25g 100g 500g



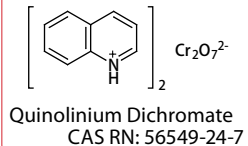
B1123 10g



P1088 5g



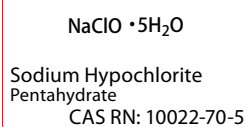
Q0058 10g 25g



次氯酸盐

Hypochlorites

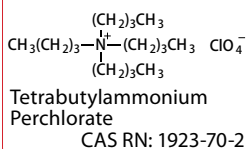
S0939 25g 500g



高氯酸盐

Perchlorates

T0836 25g 100g 500g



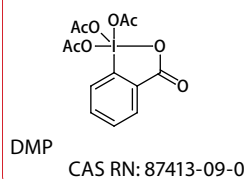
过氧化物

Peroxides

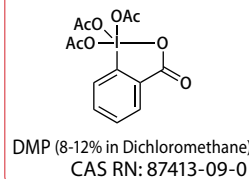
高价碘化合物

Hypervalent Iodine

D2045 1g 5g 25g



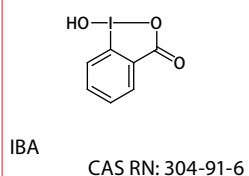
D4477 25mL 250mL



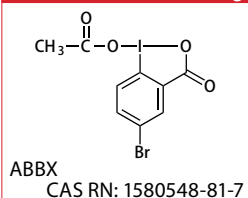
I0791 5g 25g



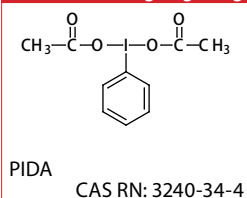
I0073 1g 10g



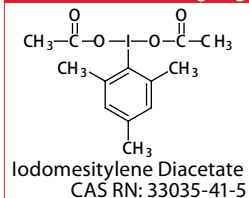
A2678 1g



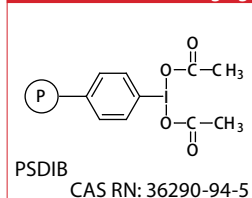
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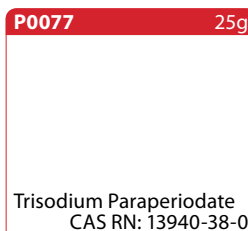
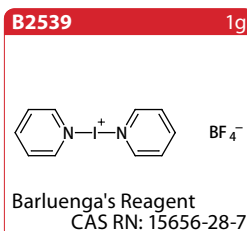
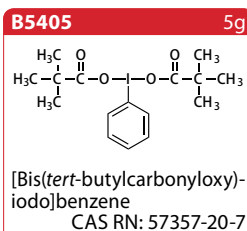
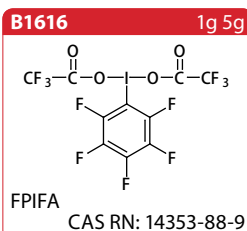


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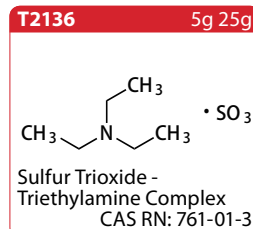
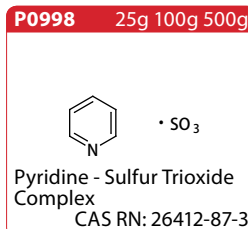
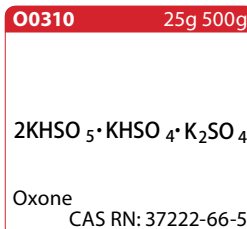


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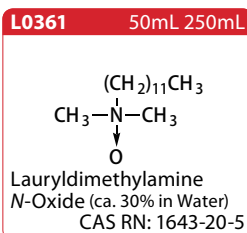
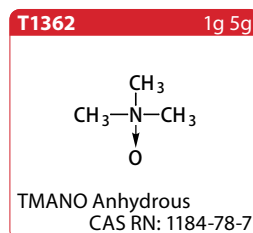
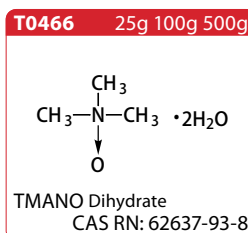
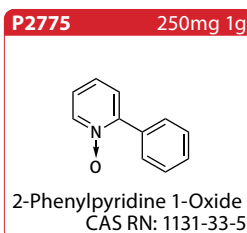
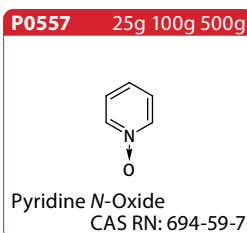
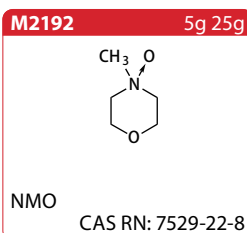
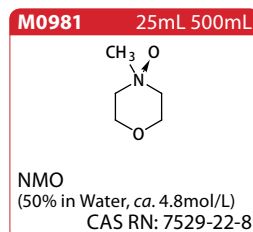
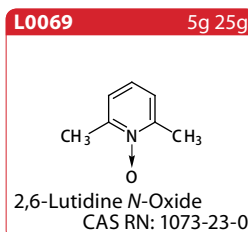
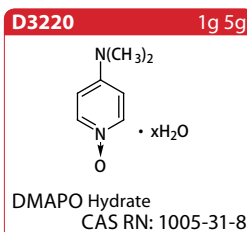
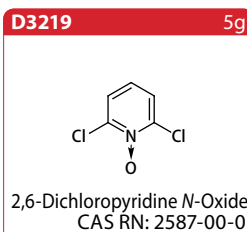
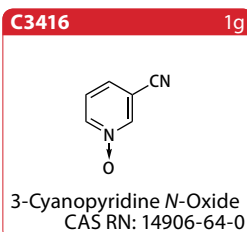
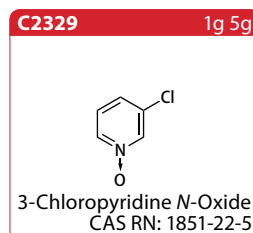
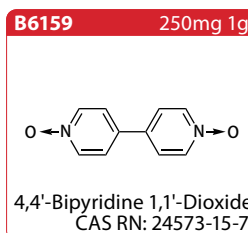
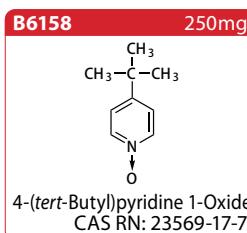




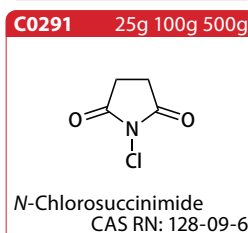
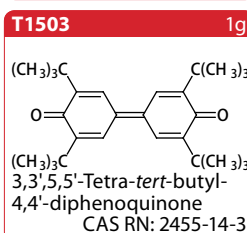
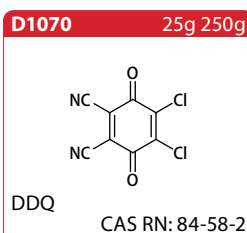
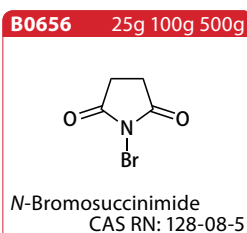
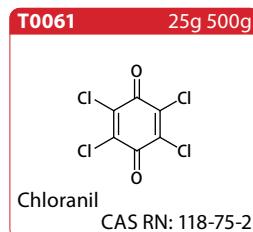
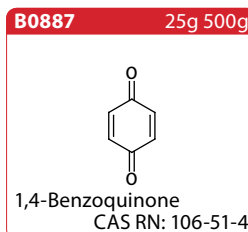
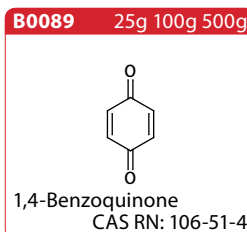
硫氧化物 Sulfur Oxides

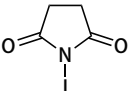
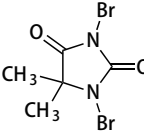
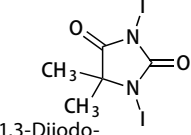
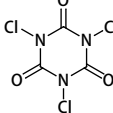
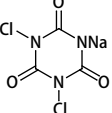
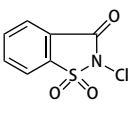
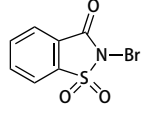
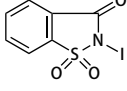
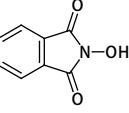
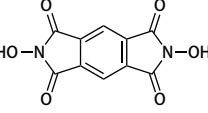
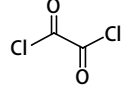
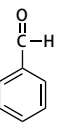
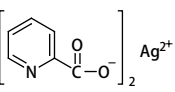
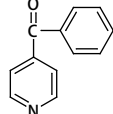
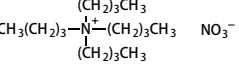
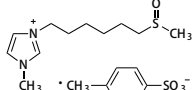
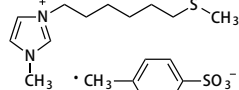
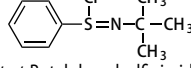
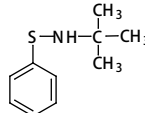
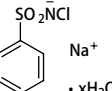
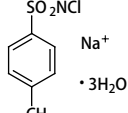
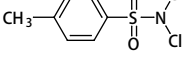
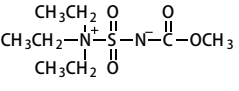
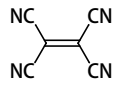
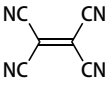
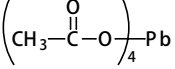
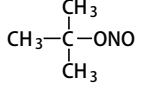
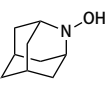
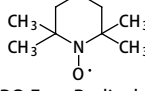
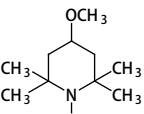


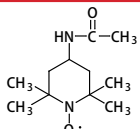
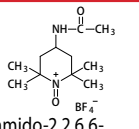
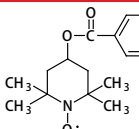
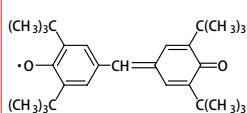
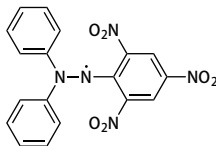
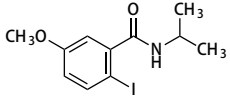
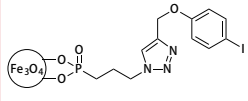
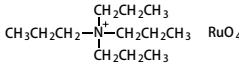
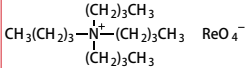
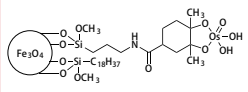
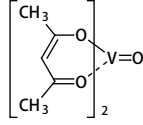
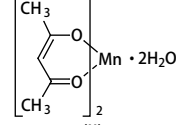
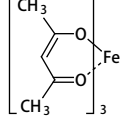
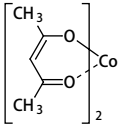
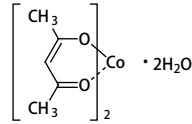
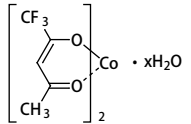
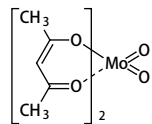
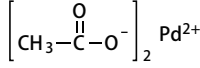
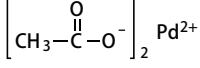
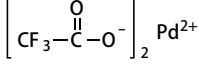
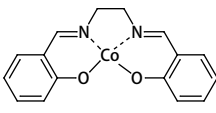
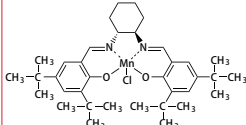
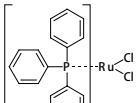
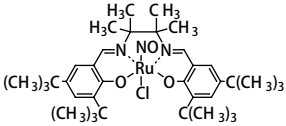
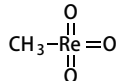
氮氧化物 N-Oxides



其它氧化剂 Other Oxidizing Agents



<p>I0074 5g 25g 100g</p>  <p>N-Iodosuccinimide CAS RN: 516-12-1</p>	<p>D1265 25g 500g</p>  <p>DBDMH CAS RN: 77-48-5</p>	<p>D3657 5g 25g</p>  <p>1,3-Diiodo-5,5-dimethylhydantoin CAS RN: 2232-12-4</p>	<p>T0620 25g 500g</p>  <p>Trichloroisocyanuric Acid CAS RN: 87-90-1</p>	<p>D1003 25g 500g</p>  <p>Sodium Dichloroisocyanurate CAS RN: 2893-78-9</p>
<p>C1674 5g 25g</p>  <p>N-Chlorosaccharin CAS RN: 14070-51-0</p>	<p>B2152 5g 25g</p>  <p>N-Bromosaccharin CAS RN: 35812-01-2</p>	<p>I0784 5g</p>  <p>N-Iodosaccharin CAS RN: 86340-94-5</p>	<p>H0395 25g 100g 500g</p>  <p>NHPI CAS RN: 524-38-9</p>	<p>D4413 1g 5g</p>  <p>NDHPI CAS RN: 57583-53-6</p>
<p>O0082 25g 100g 500g</p>  <p>Oxalyl Chloride CAS RN: 79-37-8</p>	<p>B2379 500g</p>  <p>Benzaldehyde CAS RN: 100-52-7</p>	<p>S0815 1g 5g</p>  <p>Picolinic Acid Silver(II) Salt CAS RN: 14783-00-7</p>	<p>B0306 25g</p>  <p>4-Benzoylpyridine CAS RN: 14548-46-0</p>	<p>T3651 5g 25g</p>  <p>Tetrabutylammonium Nitrate CAS RN: 1941-27-1</p>
<p>M2274 1g 5g</p>  <p>1-Methyl-3-[6-(methylsulfinyl)hexyl]imidazolium <i>p</i>-Toluenesulfonate CAS RN: 1352947-66-0</p>	<p>M2321 1g 5g</p>  <p>1-Methyl-3-[6-(methylthio)hexyl]imidazolium <i>p</i>-Toluenesulfonate CAS RN: 1352947-63-7</p>	<p>B2188 1g 5g</p>  <p><i>N</i>-<i>tert</i>-Butylphenylsulfonimidoyl Chloride CAS RN: 49591-20-0</p>	<p>B2240 1g 5g 25g</p>  <p><i>N</i>-<i>tert</i>-Butylbenzenesulfenamide CAS RN: 19117-31-8</p>	<p>C0075 25g 100g 500g</p>  <p>Chloramine B Hydrate CAS RN: 304655-80-9</p>
<p>C0076 25g 500g</p>  <p>Chloramine T Trihydrate CAS RN: 7080-50-4</p>	<p>D0318 25g 100g 500g</p>  <p>Dichloramine T CAS RN: 473-34-7</p>	<p>M1279 1g 5g 25g</p>  <p>Burgess Reagent CAS RN: 29684-56-8</p>	<p>T0077 5g 25g</p>  <p>TCNE CAS RN: 670-54-2</p>	<p>T3264 1g 5g</p>  <p>TCNE (purified by sublimation) CAS RN: 670-54-2</p>
<p>C1806 50g 500g</p> <p>(NH₄)₂Ce(NO₃)₆</p> <p>CAN CAS RN: 16774-21-3</p>	<p>E1459 25g 100g</p> <p>SeO₂</p> <p>Selenium Dioxide CAS RN: 7446-08-4</p>	<p>L0021 25g 500g</p>  <p>LTA (contains Acetic Acid) CAS RN: 546-67-8</p>	<p>P1910 25g 100g 500g</p> <p>12MoO₃ · H₃PO₄ · xH₂O</p> <p>Molybdo(VI)phosphoric Acid Hydrate CAS RN: 51429-74-4</p>	<p>N0357 25mL 250mL</p>  <p><i>tert</i>-Butyl Nitrite CAS RN: 540-80-7</p>
<p>I0604 25g 500g</p> <p>I₂</p> <p>Iodine CAS RN: 7553-56-2</p>				
<p>氧化催化剂 Catalysts for Oxidation</p>				
<p>H1404 200mg 1g 5g</p>  <p>AZADOL® CAS RN: 1155843-79-0</p>	<p>T1560 5g 25g</p>  <p>TEMPO Free Radical CAS RN: 2564-83-2</p>	<p>M1197 1g 5g</p>  <p>4-Methoxy-TEMPO Free Radical CAS RN: 95407-69-5</p>		

A1348 5g 25g  4-Acetamido-TEMPO Free Radical CAS RN: 14691-89-5	A2065 5g  4-Acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium Tetrafluoroborate CAS RN: 219543-09-6	H0878 1g 5g  4-Benzoyloxy-TEMPO Free Radical CAS RN: 3225-26-1	G0020 1g 5g  Galvinoxyl Free Radical CAS RN: 2370-18-5	D4313 1g 5g  DPPH Free Radical CAS RN: 1898-66-4
I1117 100mg  2-Iodo-N-isopropyl-5-methoxybenzamide CAS RN: 1820802-04-7	M2721 100mg  Iodobenzene Catalyst Supported on Magnetic Iron Oxide Nanoparticle (0.6-0.8mmol/g)	T1559 1g 5g  TPAP CAS RN: 114615-82-6	T1803 1g 5g  Tetrabutylammonium Perrhenate CAS RN: 16385-59-4	P1939 1g 5g KReO_4 Potassium Perrhenate CAS RN: 10466-65-6
O0308 10mL OsO_4 Osmium Tetroxide (4% in Water) CAS RN: 20816-12-0	O0414 1g  Osmium Catalyst supported on Magnetite (0.07-0.09mmol/g)	V0016 25g  Vanadyl Acetylacetonate CAS RN: 3153-26-2	M0042 25g  Manganese(II) Acetylacetonate Dihydrate CAS RN: 22033-51-8	I0079 25g 100g 500g  Acetylacetonate Iron(III) Salt CAS RN: 14024-18-1
B2681 25g  Cobalt(II) Acetylacetonate CAS RN: 14024-48-7	C0373 25g 500g  Cobalt(II) Acetylacetonate Dihydrate CAS RN: 123334-29-2	T0746 5g  Cobalt(II) Trifluoroacetylacetonate Hydrate CAS RN: 16092-38-9	M0464 5g 25g  Molybdenum(VI)dioxy Acetylacetonate CAS RN: 17524-05-9	A1424 1g 5g  Palladium(II) Acetate CAS RN: 3375-31-3
P2161 1g  Palladium(II) Acetate (Purified) CAS RN: 3375-31-3	P2106 1g 5g $[\text{Pd}(\text{CH}_3\text{COO})_2]_3$ Palladium(II) Acetate Trimer CAS RN: 53189-26-7	P1870 1g 5g  Palladium(II) Trifluoroacetate CAS RN: 42196-31-6	S0318 25g 100g 500g  Salcomine CAS RN: 14167-18-1	B5613 1g 5g  (R,R)-Jacobsen's Catalyst CAS RN: 138124-32-0
D1997 1g 5g  Tris(triphenylphosphine)-ruthenium(II) Dichloride CAS RN: 15529-49-4	C1944 100mg  Chloronitrosyl[N,N'-bis(3,5-di-tert-butylsalicylidene)-1,1,2,2-tetramethylethylenediaminato]ruthenium(IV) CAS RN: 386761-71-3	M1296 100mg  Methyltrioxorhenium(VII) CAS RN: 70197-13-6		



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