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Oxidizing Agents

Oxidation, which makes its target substance lose electrons, is one of the most basic reactions in organic chemistry and is exemplified by the combination with oxygen or a dehydrogenation reaction. In particular, oxidizing agents have often been used for the transformation of alcohols to the corresponding aldehydes, ketones or carboxylic acids. Heavy metal compounds, such as chromium(VI) oxide and potassium permanganate, have been exploited for many years. Later, less harmful oxidizing agents without heavy metals were developed, such as Dess-Martin periodinane, the Mukaiyama oxidizing agent and oxoammonium salts. Moreover, oxidation reactions employing inexpensive cooxidants have been reported in the presence of oxidation catalysts like tetrapropylammonium perruthenate (= TPAP) and TEMPO. In this way, oxidation reactions involving organic compounds have great diversity, and many books on oxidation have been published.¹⁾

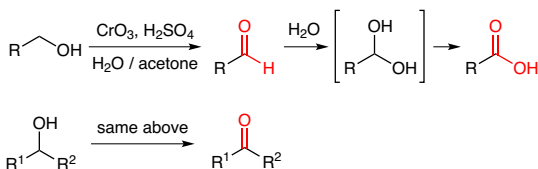
This brochure introduces a variety of oxidizing agents and catalysts for oxidation. We hope that it will be useful for your research in organic synthesis. In addition, we have prepared another brochure, "Reducing Agents", which is the reverse reaction to oxidation.

● Chromate Salts

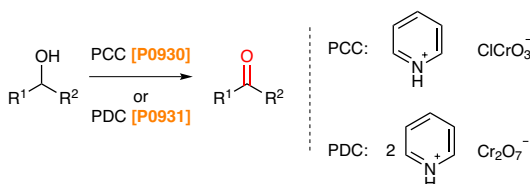
Jones *et al.* reported that a mixture of chromium oxide(VI) and diluted sulfuric acid was useful for the oxidation of alcohols, and this reaction is called Jones oxidation²⁾ It can convert primary and secondary alcohols into carboxylic acids and ketones, respectively. Since this report, chromium oxidants have been improved to develop the Sarett-Collins oxidation³⁾ process using complex chromium(VI) oxide-2py, pyridinium chlorochromate (= PCC) [P0930]⁴⁾ and pyridinium dichromate (= PDC) [P0931].⁵⁾ These reagents can oxidize primary alcohols to aldehydes without overreaction.

Caution: Chromium(VI) compounds and the chromium residue after the reaction are highly toxic, so they should be handled or discarded with consideration to the environment.

Jones oxidation

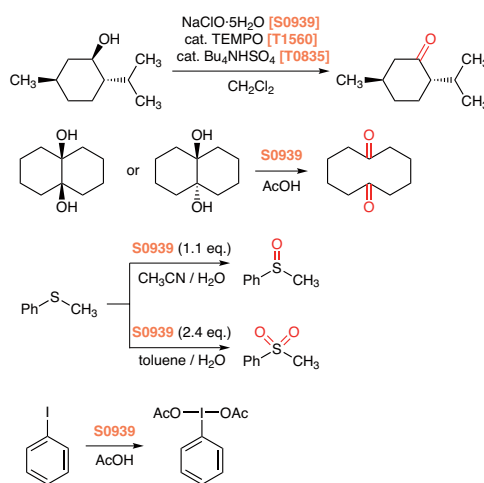


PCC and PDC oxidation



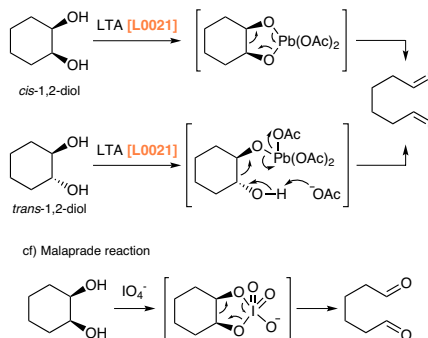
● Sodium Hypochlorite

Sodium hypochlorite pentahydrate (= NaClO·5H₂O) [S0939] is a stable crystalline solid and effective for the oxidation of hydroxy and sulfide groups. For instance, S0939 can oxidize secondary alcohols into ketones in the presence of a catalytic amount of TEMPO [T1560].⁶⁾ S0939 is also utilized in the oxidative cleavage of 1,2-diols⁷⁾ and oxidation of sulfides.⁸⁾ Sulfoxides and sulfones can be synthesized in high yields by adjusting the equivalents of S0939. Furthermore, it has recently been reported that S0939 is useful for the convenient synthesis of hypervalent iodine compounds.⁹⁾



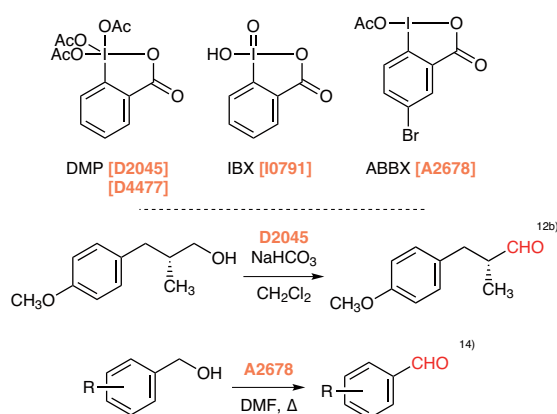
● Criegee Oxidation

Criegee oxidation gives two ketones or aldehydes from 1,2-diols by using lead(IV) tetraacetate (= LTA) [L0021] as an oxidant.¹⁰⁾ This reaction is different from the oxidative cleavage reaction using periodate salt (= Malprade reaction)¹¹⁾ and proceeds when applied to *trans*-1,2-diols, which would be difficult to pass through the five-membered intermediate. This indicates another reaction mechanism that does not pass through the cyclic transition state.



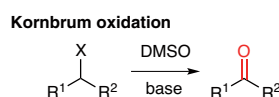
● Oxidation using Hypervalent Iodine Compounds

Dess-Martin periodinane (= DMP)¹²⁾ [D2045] [D4477] can oxidize primary and secondary alcohols into aldehydes and ketones, respectively. DMP has some advantages compared with chromate(VI) compounds: the reaction using DMP proceeds under mild conditions; the generality of reactive substrates is wide; the environmental impact is lower; and the treatment after the reaction is easy. 2-Iodoxybenzoic acid (= IBX)¹³⁾ [I0791] and 1-acetoxy-5-bromo-1,2-benziodoxol-3(1*H*)-one (= ABBX)¹⁴⁾ [A2678], which was developed by Togo, are also utilized as oxidants of alcohols as well as other hypervalent iodine compounds.¹⁵⁾ These compounds are introduced in our brochure "Hypervalent Iodine Compounds".



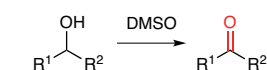
● DMSO Oxidations and Odorless Swern Oxidants

Kornblum *et al.* found that the carbonyl group was produced from benzyl halides and tosylates by the treatment of DMSO [D0798] in the presence of a base.¹⁶⁾ After this report, various types of oxidations using DMSO have been reported as follows: Pfitzner-Moffatt oxidation¹⁷⁾ using DCC [D0436]; Albright-Goldman oxidation¹⁸⁾ using acetic anhydride [A2036]; Parikh-Doering oxidation¹⁹⁾ using SO₃-pyridine complex [P0998]; and Swern oxidation²⁰⁾ using oxalyl chloride [O0082]. These reactions are



X = halogen, TsO

Various DMSO oxidations

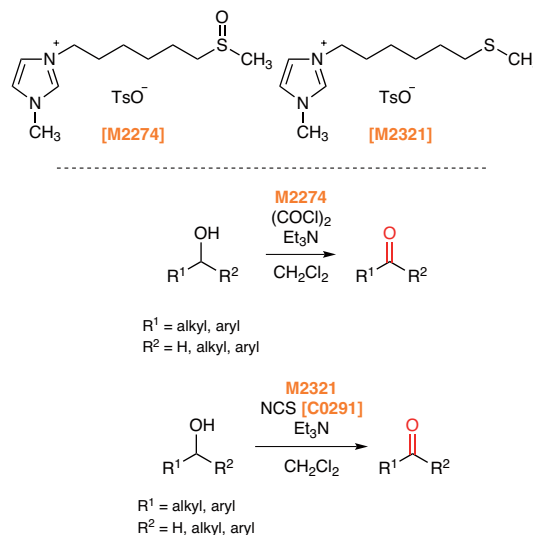


R¹ = alkyl, aryl
R² = H, alkyl, aryl

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]

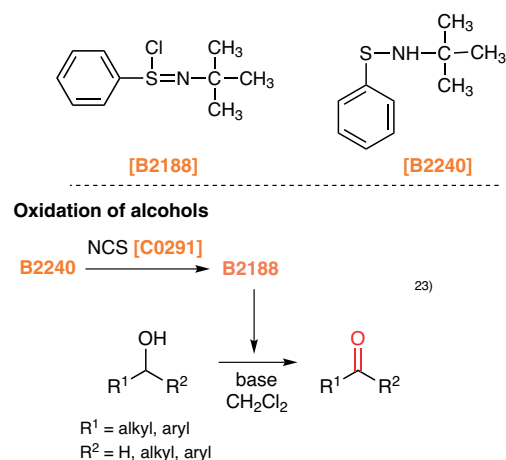
utilized widely from the laboratory scale to the industrial scale.

One problem with DMSO oxidation is the odor of the byproduct dimethyl sulfide. To solve this problem, Togo *et al.* developed the odorless and recyclable imidazolium salts [M2274] and [M2321] for use in Swern oxidation^{21a)} and Corey-Kim oxidation,^{21b)} respectively.

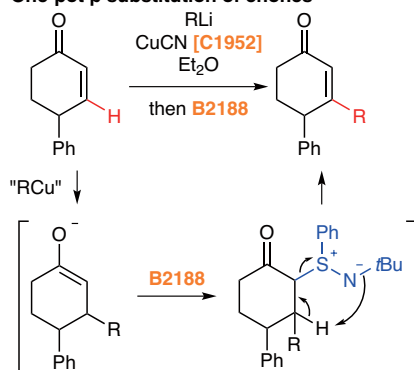


● Mukaiyama Oxidation Reaction

Mukaiyama's group reported two new oxidation reactions using *N*-*tert*-butylbenzenesulfinimidoyl chloride [B2188],²²⁾ and catalytic amounts of *N*-*tert*-butylbenzenesulfenamide [B2240] and NCS [C0291],²³⁾ respectively. It is considered that B2188 is generated *in situ* by the reaction of B2240 and NCS, and turns into B2240 after the reaction; thus B2240 works as a catalyst. B2188 is a stable solid and can give α,β -unsaturated ketones from an enolate by deprotonation at the α -position or 1,4-addition.²⁴⁾ In addition, the new method has been reported to afford a ketone from an aldehyde, an alkyllithium and B2188 in one pot.²⁵⁾



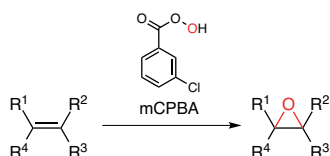
One-pot β -substitution of enones²⁴⁾



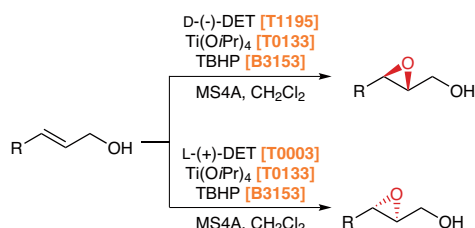
Epoxidation Reaction

Epoxidation is also an oxidation reaction and the Prilezhaev (Prileschajew) reaction²⁶⁾ with mCPBA is regarded as a representative epoxidation. Furthermore, asymmetric epoxidation reactions have been reported such as Sharpless-Katsuki asymmetric epoxidation²⁷⁾ for allyl alcohols and Jacobsen-Katsuki asymmetric epoxidation²⁸⁾ of *cis*-olefins. Sharpless-Katsuki asymmetric epoxidation is often used in the total syntheses of natural products.

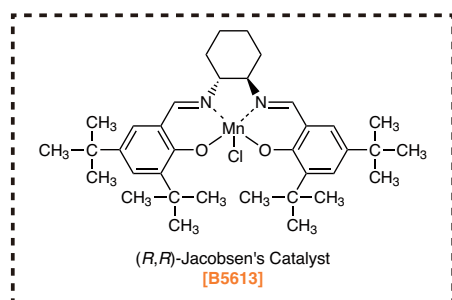
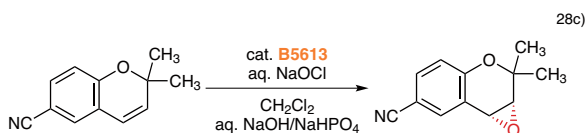
Prilezhaev epoxidation



Sharpless-Katsuki asymmetric epoxidation



Jacobsen-Katsuki asymmetric epoxidation

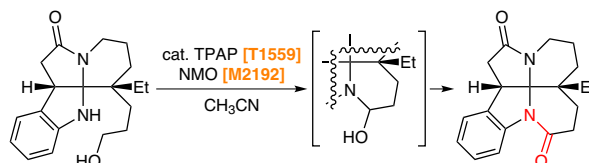
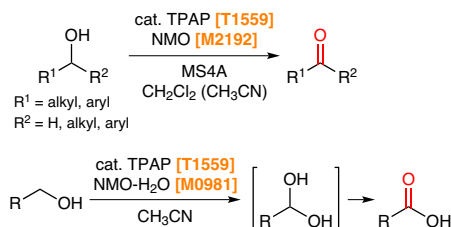


Catalytic Oxidation Reactions

1. Oxidation with TPAP Catalyst

Tetrapropylammonium perruthenate (= TPAP) [T1559] catalyst can oxidize alcohols into aldehydes and ketones by the addition of 4-methylmorpholine *N*-oxide (= NMO) [M2192] as a cooxidant (Ley-Griffith oxidation).²⁹⁾ This reaction proceeds under very mild conditions to give the corresponding product in high yield even when applied to unstable substances. Moreover, this reaction can oxidize primary alcohols to carboxylic acids in the presence of water by hydration of the aldehyde to form a *gem*-diol and subsequent reoxidation.³⁰⁾ TPAP and NMO are often applied in the syntheses of natural products. Gaich's group, for instance, have reported the total synthesis of (-)-leuconoxine by ingeniously applying this reaction at the last step.³¹⁾

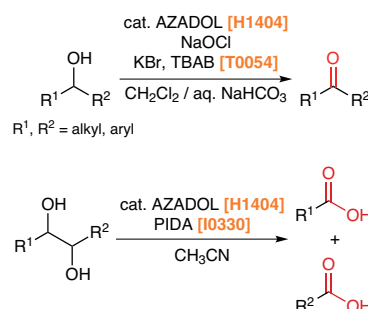
Ley-Griffith oxidation



2. Oxidation Using AZADOL®

AZADOL® [H1404], known as the precursor of an oxidation catalyst, is a hydroxyamine developed by Iwabuchi *et al.*³²⁾ The oxidizing ability of H1404 is superior to that of TEMPO [T1560], particularly for secondary alcohols. In addition, 1,2-diols are oxidatively cleaved by the treatment of a catalytic amount of PIDA [I0330] to afford two carboxylic acids. H1404 is anticipated as a green catalyst for oxidation since sodium hypochlorite, sodium chlorite and even oxygen in air can be utilized as cooxidants.

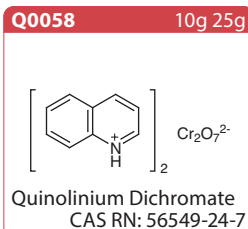
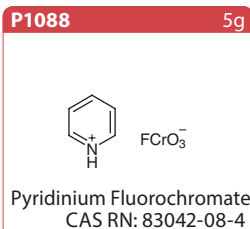
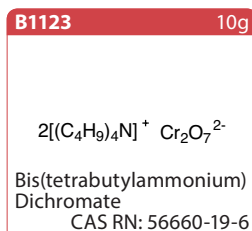
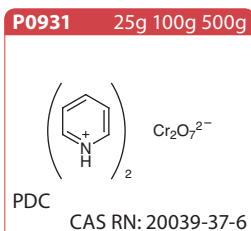
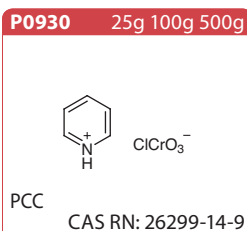
AZADOL® is a registered trademark of Nissan Chemical Corporation.



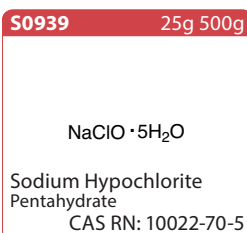
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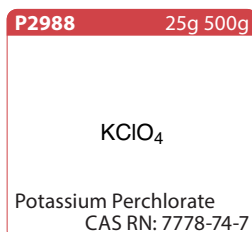
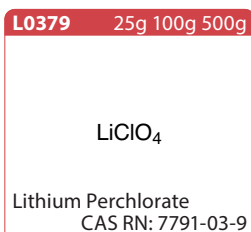
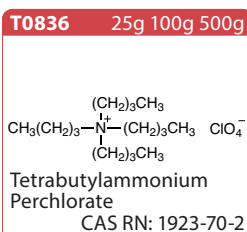
Chromates



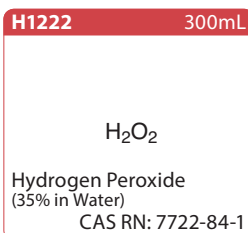
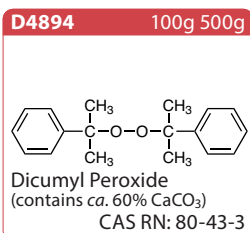
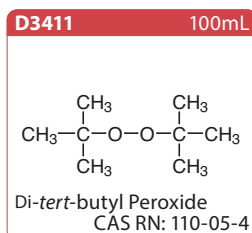
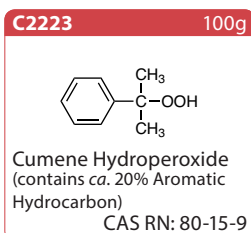
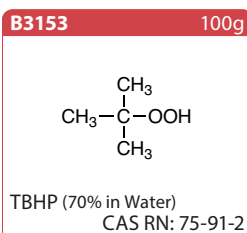
Hypochlorites



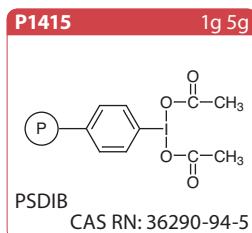
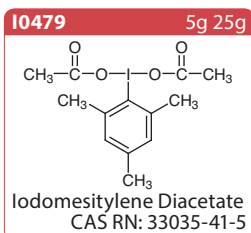
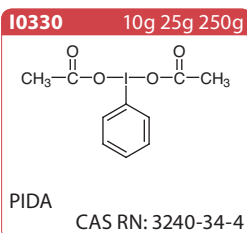
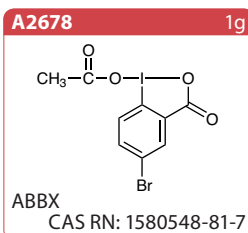
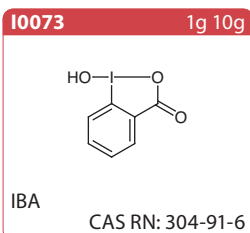
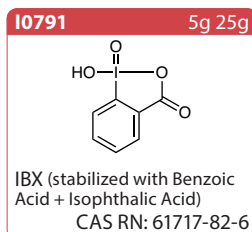
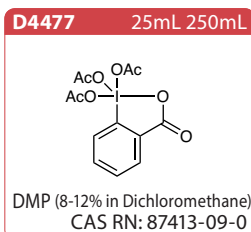
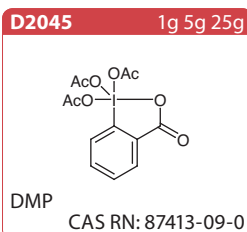
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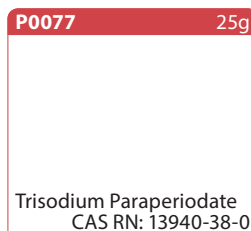
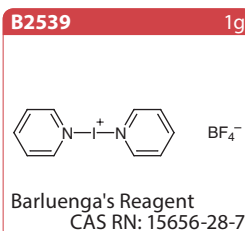
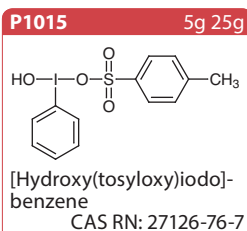
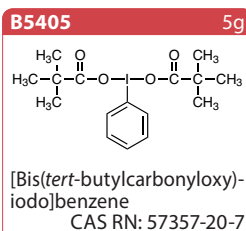
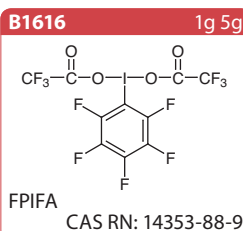


Peroxides

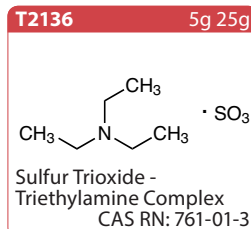
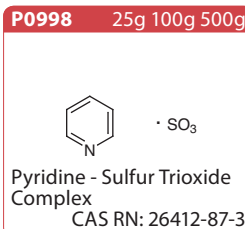
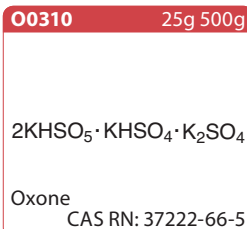


Hypervalent Iodine

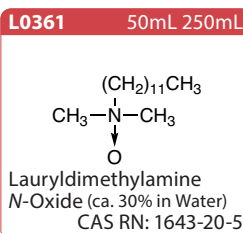
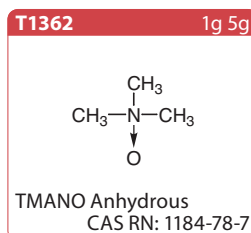
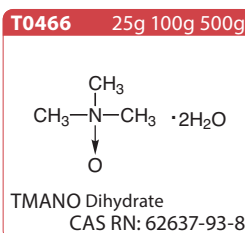
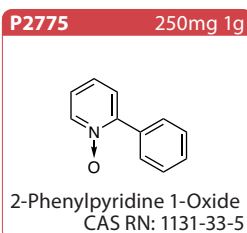
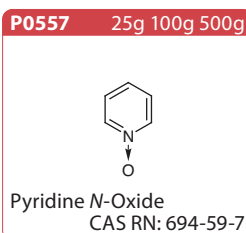
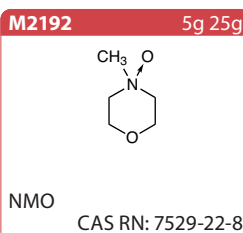
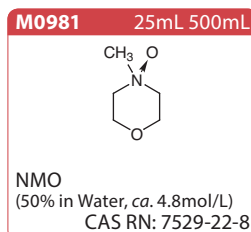
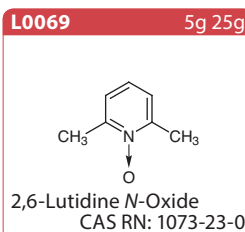
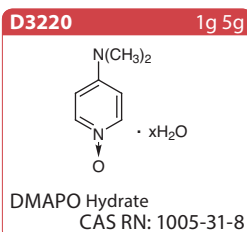
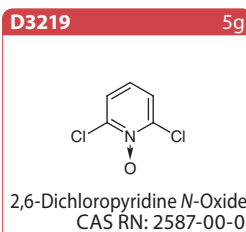
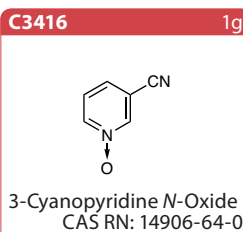
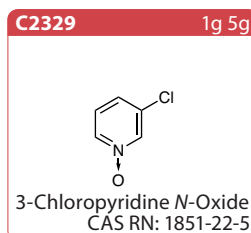
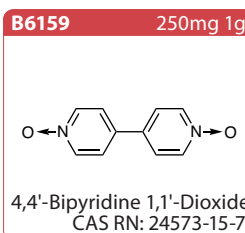
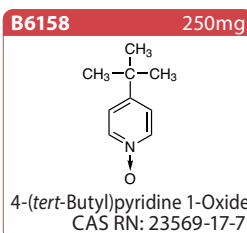




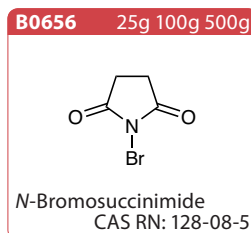
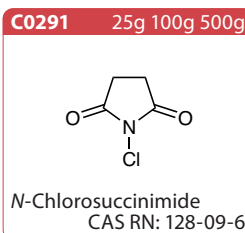
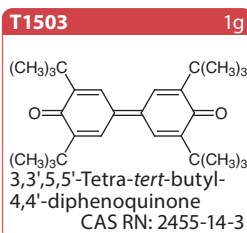
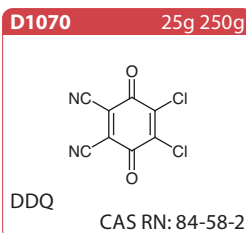
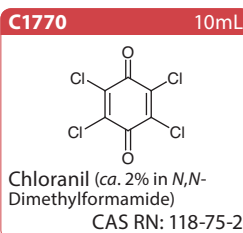
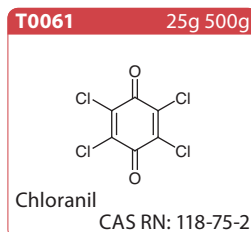
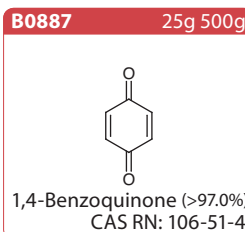
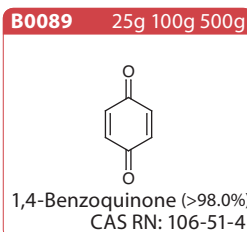
Sulfur Oxides



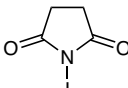
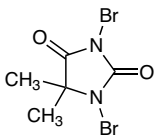
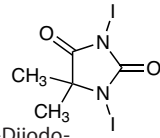
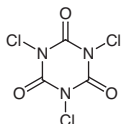
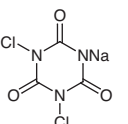
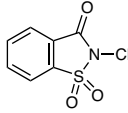
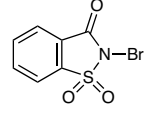
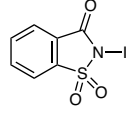
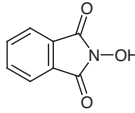
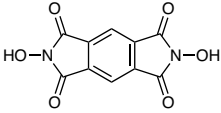
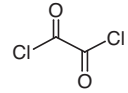
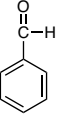
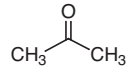
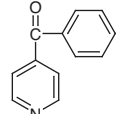
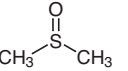
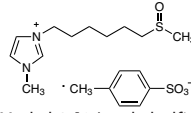
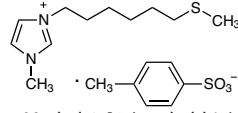
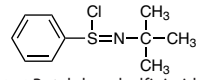
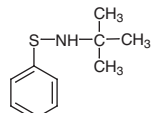
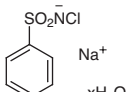
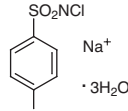
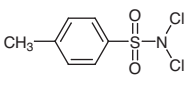
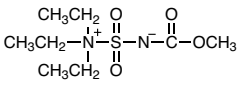
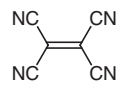
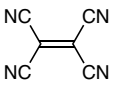
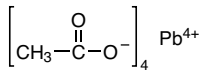
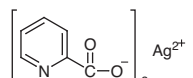
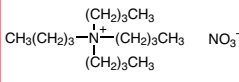
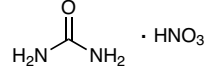
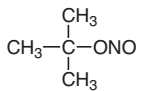
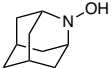
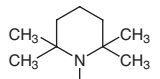
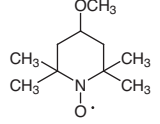
N-Oxides

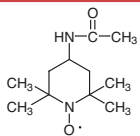
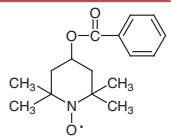
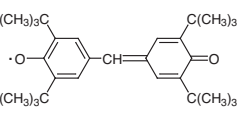
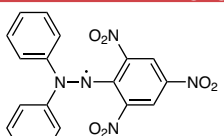
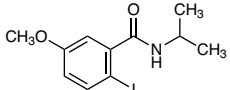
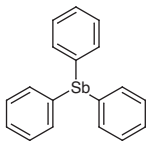
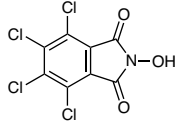
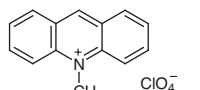
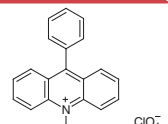
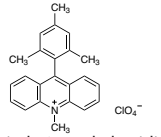
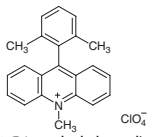
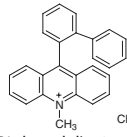
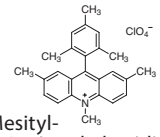
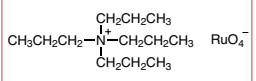
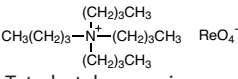
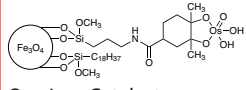
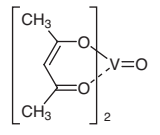
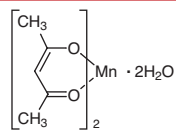
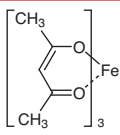
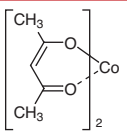
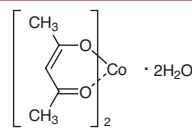
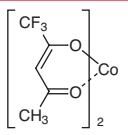
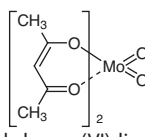
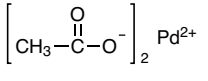
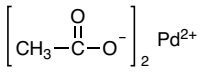
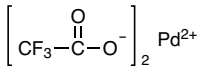
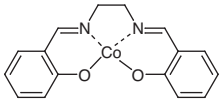
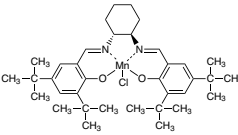
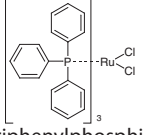
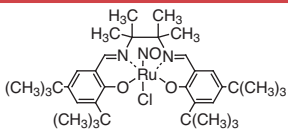
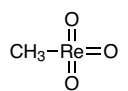


Other Oxidizing Agents



Oxidizing Agents

I0074 5g 25g 100g  N-Iodosuccinimide CAS RN: 516-12-1	D1265 25g 500g  DBDMH CAS RN: 77-48-5	D3657 5g 25g  1,3-Diiodo-5,5-dimethylhydantoin CAS RN: 2232-12-4	T0620 25g 500g  Trichloroisocyanuric Acid CAS RN: 87-90-1	D1003 25g 500g  Sodium Dichloroisocyanurate CAS RN: 2893-78-9	
C1674 5g 25g  N-Chlorosaccharin CAS RN: 14070-51-0	B2152 5g 25g  N-Bromosaccharin CAS RN: 35812-01-2	I0784 5g  N-Iodosaccharin CAS RN: 86340-94-5	H0395 25g 100g 500g  NHPI CAS RN: 524-38-9	D4413 1g 5g  NDHPI CAS RN: 57583-53-6	
O0082 25g 100g 500g  Oxalyl Chloride CAS RN: 79-37-8	B2379 500g  Benzaldehyde CAS RN: 100-52-7	A0054 500mL  Acetone CAS RN: 67-64-1	B0306 25g  4-Benzoylpyridine CAS RN: 14548-46-0	D0798 25g 500g  Dimethyl Sulfoxide CAS RN: 67-68-5	
M2274 1g 5g  1-Methyl-3-[6-(methylsulfinyl)-hexyl]imidazolium <i>p</i> -Toluenesulfonate CAS RN: 1352947-66-0	M2321 1g 5g  1-Methyl-3-[6-(methylthio)-hexyl]imidazolium <i>p</i> -Toluenesulfonate CAS RN: 1352947-63-7	B2188 1g 5g  <i>N</i> - <i>tert</i> -Butylphenylsulfonimidoyl Chloride CAS RN: 49591-20-0	B2240 1g 5g 25g  <i>N</i> - <i>tert</i> -Butylbenzenesulfenamide CAS RN: 19117-31-8	C0075 25g 100g 500g  Chloramine B Hydrate CAS RN: 304655-80-9	
C0076 25g 500g  Chloramine T Trihydrate CAS RN: 7080-50-4	D0318 25g 100g 500g  Dichloramine T CAS RN: 473-34-7	M1279 1g 5g 25g  Burgess Reagent CAS RN: 29684-56-8	T0077 5g 25g  TCNE CAS RN: 670-54-2	T3264 1g 5g  TCNE (purified by sublimation) CAS RN: 670-54-2	
C1806 50g 500g (NH ₄) ₂ Ce(NO ₃) ₆ CAN CAS RN: 16774-21-3	E1459 25g 100g SeO ₂ Selenium Dioxide CAS RN: 7446-08-4	L0021 25g 500g  LTA (contains Acetic Acid) CAS RN: 546-67-8	P1910 25g 100g 500g 12MoO ₃ · H ₃ PO ₄ · xH ₂ O Molybdo(VI)phosphoric Acid Hydrate CAS RN: 51429-74-4	S0815 1g 5g  Picolinic Acid Silver(II) Salt CAS RN: 14783-00-7	
T3651 5g 25g  Tetrabutylammonium Nitrate CAS RN: 1941-27-1	U0015 25g  Urea Nitrate (wetted with ca. 25% Water) (unit weight on dry weight basis) CAS RN: 124-47-0	N0357 25mL 250mL  <i>tert</i> -Butyl Nitrite CAS RN: 540-80-7	B2414 90g 500g Br ₂ Bromine CAS RN: 7726-95-6	I0604 25g 500g I ₂ Iodine CAS RN: 7553-56-2	
Catalysts for Oxidation			H1404 200mg 1g 5g  AZADOL® CAS RN: 1155843-79-0	T1560 5g 25g  TEMPO Free Radical CAS RN: 2564-83-2	M1197 1g 5g  4-Methoxy-TEMPO Free Radical CAS RN: 95407-69-5

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	T0476 25g  Triphenylantimony CAS RN: 603-36-1	H1765 1g 5g  TCNHP CAS RN: 85342-65-0	M1787 250mg 1g  10-Methylacridinium Perchlorate CAS RN: 26456-05-3	M1775 1g 5g  10-Methyl-9-phenylacridinium Perchlorate CAS RN: 36519-61-6
M1774 1g 5g  9-Mesityl-10-methylacridinium Perchlorate CAS RN: 674783-97-2	D3429 1g  9-(2,6-Dimethylphenyl)-10-methylacridinium Perchlorate CAS RN: 1276539-32-2	B2897 1g 5g  9-(2-Biphenyl)-10-methylacridinium Perchlorate CAS RN: 2743539-91-3	M2072 1g  9-Mesityl-2,7,10-trimethylacridinium Perchlorate CAS RN: 1216909-33-9	T1559 1g 5g  TPAP CAS RN: 114615-82-6
T1803 1g 5g  Tetrabutylammonium Perrhenate CAS RN: 16385-59-4	P1939 1g 5g  Potassium Perrhenate CAS RN: 10466-65-6	O0308 10mL  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 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	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-tetramethylethylenediamine]ruthenium(IV) CAS RN: 386761-71-3	M1296 100mg  Methyltrioxorhenium(VII) CAS RN: 70197-13-6	

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