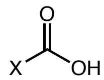
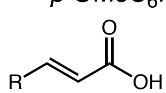
pKa's of Inorganic and Oxo-Acids

INORGANIC ACIDS

Substrate	pKa H_2O	(DMSO)
H_2O	15.7	(32)
H_3O^+	-1.7	
H_2S	7.00	
HBr	-9.00	(0.9)
HCl	-8.0	(1.8)
HF	3.17	(15)
HOCl	7.5	
$HClO_4$	-10	
HCN	9.4	(12.9)
HN_3	4.72	(7.9)
HSCN	4.00	
H_2SO_3	1.9, 7.21	
H_2SO_4	-3.0, 1.99	
H_3PO_4	2.12, 7.21, 12.32	
HNO_3	-1.3	
HNO_2	3.29	
H_2CrO_4	-0.98, 6.50	
CH_3SO_3H	-2.6	(1.6)
CF_3SO_3H	-14	(0.3)
NH_4Cl	9.24	
$B(OH)_3$	9.23	
HOOH	11.6	

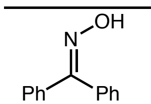
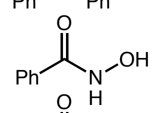
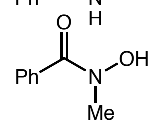
CARBOXYLIC ACIDS

Substrate	pKa H_2O	(DMSO)
		
X= CH_3	4.76	(12.3)
CH_2NO_2	1.68	
CH_2F	2.66	
CH_2Cl	2.86	
CH_2Br	2.86	
CH_2I	3.12	
$CHCl_2$	1.29	
CCl_3	0.65	
CF_3	-0.25	
H	3.77	
HO	3.6, 10.3	
C_6H_5	4.2	(11.1)
o-$O_2NC_6H_4$	2.17	
m-$O_2NC_6H_4$	2.45	
p-$O_2NC_6H_4$	3.44	
o-ClC_6H_4	2.94	
m-ClC_6H_4	3.83	
p-ClC_6H_4	3.99	
o-$(CH_3)_3N^+C_6H_4$	1.37	
p-$(CH_3)_3N^+C_6H_4$	3.43	
p-$OMeC_6H_4$	4.47	
		
R= H	4.25	
trans-CO_2H	3.02, 4.38	
cis-CO_2H	1.92, 6.23	

ALCOHOLS

Substrate	pKa H_2O	(DMSO)
HOH	15.7	(31.2)
MeOH	15.5	(27.9)
i-PrOH	16.5	(29.3)
t-BuOH	17.0	(29.4)
c-hex_3COH	24.0	
CF_3CH_2OH	12.5	(23.5)
$(CF_3)_2CHOH$	9.3	(18.2)
C_6H_5OH	9.95	(18.0)
m-$O_2NC_6H_4OH$	8.4	
p-$O_2NC_6H_4OH$	7.1	(10.8)
p-$OMeC_6H_4OH$	10.2	(19.1)
2-napthol		(17.1)

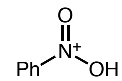
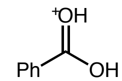
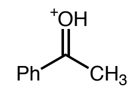
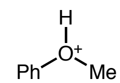
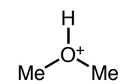
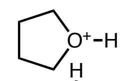
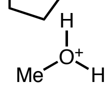
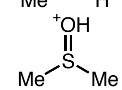
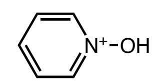
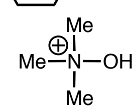
OXIMES & HYDROXAMIC ACIDS

Substrate	pKa H_2O	(DMSO)
	11.3	(20.1)
	8.88 (NH)	(13.7)
		(18.5)

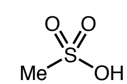
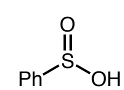
PEROXIDES

Substrate	pKa H_2O	(DMSO)
MeOOH	11.5	
CH_3CO_3H	8.2	

PROTONATED SPECIES

Substrate	pKa H_2O	(DMSO)
	-12.4	
	-7.8	
	-6.2	
	-6.5	
	-3.8	
	-2.05	
	-2.2	
	-1.8	
	0.79	(+1.63)
		(+5.55)

SULFINIC & SULFONIC ACIDS

Substrate	pKa H_2O	(DMSO)
	-2.6	
	2.1	

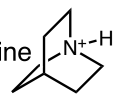
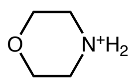
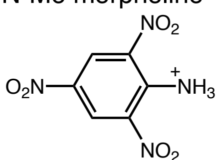
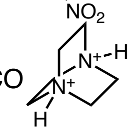
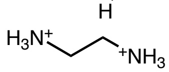
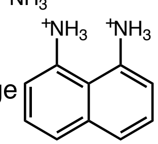
*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

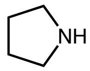
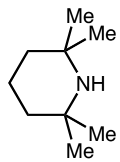
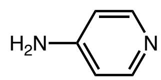
pKa's of Nitrogen Acids

Substrate pKa H_2O (DMSO)

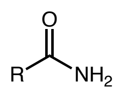
PROTONATED NITROGEN

Substrate	pKa H_2O	(DMSO)
N^+H_4	9.2	(10.5)
EtN^+H_3	10.6	
i-$Pr_2N^+H_2$	11.05	
Et_3N^+H	10.75	(9.00)
PhN^+H_3	4.6	(3.6)
$PhN^+(Me)_2H$	5.20	(2.50)
$Ph_2N^+H_2$	0.78	
2-napthal-N^+H_3	4.16	
$H_2NN^+H_3$	8.12	
HON^+H_3	5.96	
Quinuclidine 	11.0	(9.80)
Morpholine 	8.36	
N-Me morpholine	7.38	
	-9.3	
DABCO 	2.97, 8.82 (2.97, 8.93)	
	6.90, 9.95	
Proton Sponge 	-9.0, 12.0 (--, 7.50)	
$PhCN^+H$	-10	

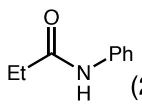
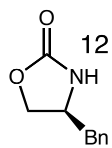
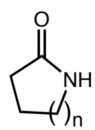
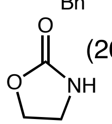
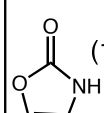
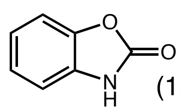
AMINES

Substrate	pKa H_2O	(DMSO)
HN_3	4.7	(7.9)
NH_3	38	(41)
i-Pr_2NH	(36 THF))	
TMS_2NH	26(THF)	(30)
$PhNH_2$		(30.6)
Ph_2NH		(25.0)
$NCNH_2$		(16.9)
		(44)
		(37)
		(26.5)

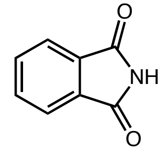
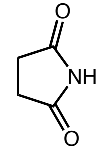
AMIDES & CARBAMATES



R=	pKa H_2O	(DMSO)
H		(23.5)
CH_3	15.1	(25.5)
Ph		(23.3)
CF_3		(17.2)
(urea) NH_2		(26.9)
OEt		(24.8)

Substrate	pKa H_2O	(DMSO)
		(21.6)
	12	(20.5)
		n= 1 (24.1) n= 2 (26.4)
		(20.8)
		(15)
		(12.1)

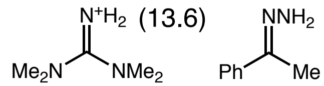
IMIDES

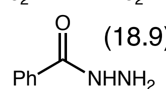
Substrate	pKa H_2O	(DMSO)
	8.30	
		(14.7)
Ac_2NH		(17.9)

SULFONAMIDE

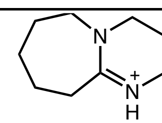
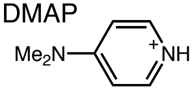
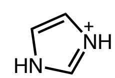
Substrate	pKa H_2O	(DMSO)
RSO_2NH_2 R = Me		(17.5)
Ph		(16.1)
CF_3	6.3	(9.7)
$MeSO_2NHPh$		(12.9)

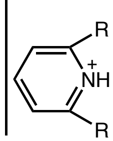
GUANIDINIUM, HYRDAZONES,- IDES, & -INES



Substrate	pKa H_2O	(DMSO)
guanidinium (N^+H_2)		(13.6)
hydrazone (NNH_2)		(21.6)
		(18.9)
$PhSO_2NHNH_2$		(17.2)
PhNHNHPh		(26.1)

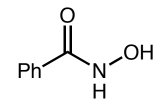
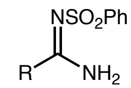
PROTONATED HETEROCYCLES

Substrate	pKa H_2O	(DMSO)
DBU 	(12) (estimate)	
DMAP 	9.2	
	6.95	

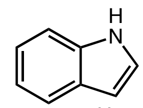
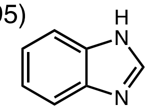
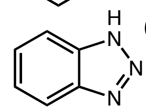
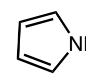
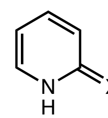
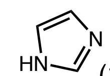
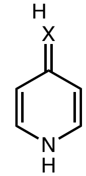
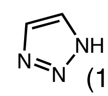
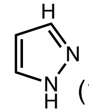
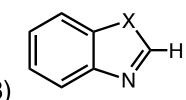
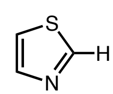
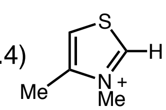
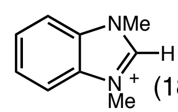
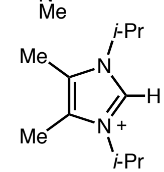


R=	pKa H_2O	(DMSO)
H (PPTS)	5.21	(3.4)
t-Bu	4.95	(0.90)
Me	6.75	(4.46)
Cl, H	0.72	

HYDROXAMIC ACID & AMIDINES

Substrate	pKa H_2O	(DMSO)
	8.88 (NH)	(13.7)
 R= Me		(17.3)
Ph		(15.0)

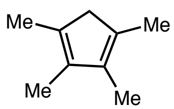
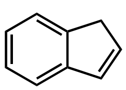
HETEROCYCLES

Substrate	pKa H_2O	(DMSO)
		(20.95)
		(16.4)
		(11.9)
		(23.0)
		X= O (24) X= S (13.3)
		(18.6)
		X= O (14.8) X= S (11.8)
		(13.9)
		(19.8)
		X= O (24.4) X= S (27.0)
		(29.4)
		(16.5)
		(18.4)
		(24)

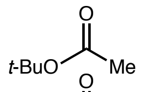
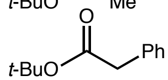
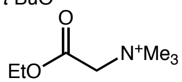
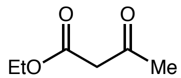
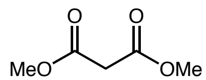
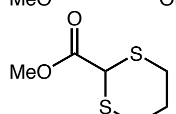
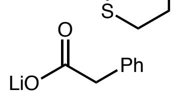
*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

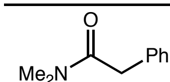
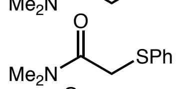
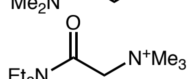
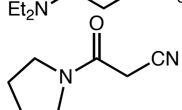
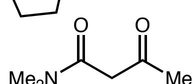
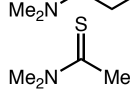
HYDROCARBONS

Substrate	pKa H_2O	(DMSO)
$(Me)_3CH$	53	
$(Me)_2CH_2$	51	
$CH_2=CH_2$	50	
CH_4	48	(56)
	46	
$CH_2=CHCH_3$	43	(44)
PhH	43	
$PhCH_3$	41	(43)
Ph_2CH_2	33.5	(32.2)
Ph_3CH	31.5	(30.6)
HCCH	24	
PhCCH	23	(28.8)
$XC_6H_4CH_3$		
X= *p*-CN		(30.8)
p-NO_2		(20.4)
p-COPh		(26.9)
		(26.1)
	20	(20.1)
	15	(18.0)
H_2	~36	

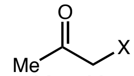
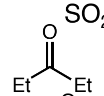
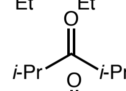
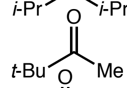
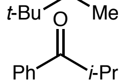
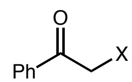
ESTERS

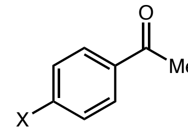
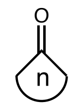
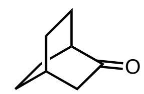
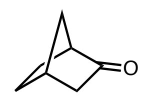
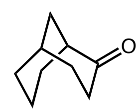
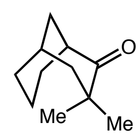
Substrate	pKa H_2O	(DMSO)
	24.5	(30.3)
		(23.6)
		(20.0)
	11	(14.2)
	13	(15.7)
		(20.9)
		[30.2 (THF)]

AMIDES

Substrate	pKa H_2O	(DMSO)
		(26.6)
		(25.9)
		(24.9)
		(17.2)
		(18.2)
		(25.7)

KETONES

Substrate	pKa H_2O	(DMSO)
		
X= H		(26.5)
Ph		(19.8)
SPh		(18.7)
$COCH_3$	9	(13.3)
SO_2Ph		(12.5)
	19-20	(27.1)
		(28.3)
		(27.7)
		(26.3)
		
X= H		(24.7)
CH_3		(24.4)
Ph		(17.7)
$COCH_3$		(14.2)
COPh		(13.3)
CN		(10.2)
F		(21.6)
OMe		(22.85)
OPh		(21.1)
SPh		(16.9)
SePh		(18.6)
NPh_2		(20.3)
N^+Me_3		(14.6)
NO_2		(7.7)
SO_2Ph		(11.4)

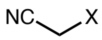
Substrate	pKa H_2O	(DMSO)
		
X= H		(24.7)
OMe		(25.7)
NMe_2		(27.5)
Br		(23.8)
CN		(22.0)
		
n= 4		(25.1)
5		(25.8)
6		(26.4)
7		(27.7)
8		(27.4)
		(28.1)
		(29.0)
		(25.5)
		(32.4)

*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

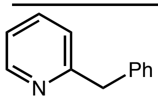
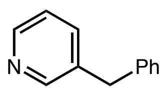
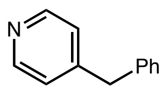
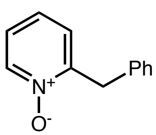
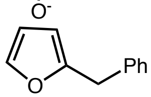
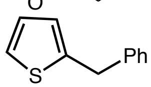
pKa's of CH bonds at Nitrile, Heteroaromatic, and Sulfur Substituted Carbon

NITRILES

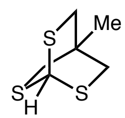
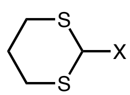


Substrate	pKa H_2O	(DMSO)
X= H		(31.3)
CH_3		(32.5)
Ph		(21.9)
COPh		(10.2)
$CONR_2$		(17.1)
CO_2Et		(13.1)
CN	11	(11.1)
OPh		(28.1)
N^+Me_3		(20.6)
SPh		(20.8)
SO_2Ph		(12.0)

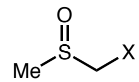
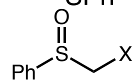
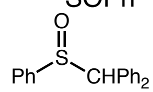
HETERO-AROMATICS

Substrate	pKa H_2O	(DMSO)
		(28.2)
		(30.1)
		(26.7)
		(25.2)
		(30.2)
		(30.0)

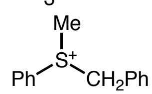
SULFIDES

Substrate	pKa H_2O	(DMSO)
$PhSCH_2X$		
X= Ph		(30.8)
CN		(20.8)
$COCH_3$		(18.7)
COPh		(16.9)
NO_2		(11.8)
SPh		(30.8)
SO_2Ph		(20.5)
SO_2CF_3		(11.0)
$POPh_2$		(24.9)
$MeSCH_2SO_2Ph$		(23.4)
$PhSCHPh_2$		(26.7)
$(PhS)_3CH$		(22.8)
$(PrS)_3CH$		(31.3)
		(30.5)
$(PhS)_2CHPh$		(23.0)
		
X= Ph		(30.7)
CO_2Me		(20.8)
CN		(19.1)
$RSCH_2CN$		
R= Me		(24.3)
Et		(24.0)
i-Pr		(23.6)
t-Bu		(22.9)
$PhSCH=CHCH_2SPh$		(26.3)
BuSH	10-11	(17.0)
PhSH	≈7	(10.3)

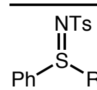
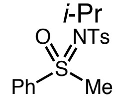
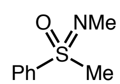
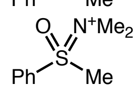
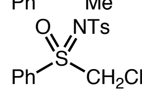
SULFOXIDES

Substrate	pKa H_2O	(DMSO)
		
X= H		(35.1)
Ph		(29.0)
SPh		(29.0)
		
X= H		(33)
Ph		(27.2)
SOPh		(18.2)
		(24.5)

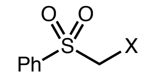
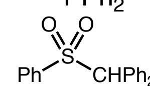
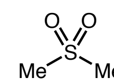
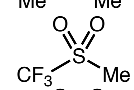
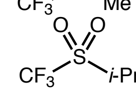
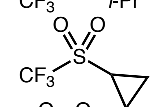
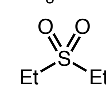
SULFONIUM

Substrate	pKa H_2O	(DMSO)
$Me_3S^+=O$		(18.2)
		(16.3)

SULFIMIDES & SULFOXIMINES

Substrate	pKa H_2O	(DMSO)
		
R= Me		(27.6)
i-Pr		(30.7)
		(24.5)
		(33)
		(14.4)
		(20.7)

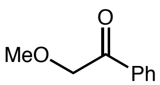
SULFONES

Substrate	pKa H_2O	(DMSO)
		
X= H		(29.0)
CH_3		(31.0)
t-Bu		(31.2)
Ph		(23.4)
$CH=CH_2$		(22.5)
CH=CHPh		(20.2)
CCH		(22.1)
CCPh		(17.8)
COPh		(11.4)
COMe		(12.5)
OPh		(27.9)
N^+Me_3		(19.4)
CN		(12.0)
NO_2		(7.1)
SMe		(23.5)
SPh		(20.5)
SO_2Ph		(12.2)
PPh_2		(20.2)
		(22.3)
		(31.1)
		(18.8)
		(21.8)
		(26.6)
		(32.8)
$(PhSO_2)_2CH_2Me$		(14.3)

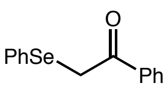
*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

pKa's of CH bonds at Heteroatom Substituted Carbon & References

ETHERS

Substrate	pKa H_2O	(DMSO)
CH_3OPh		(49)
$MeOCH_2SO_2Ph$		(30.7)
$PhOCH_2SO_2Ph$		(27.9)
$PhOCH_2CN$		(28.1)
		(22.85)

SELENIDES

Substrate	pKa H_2O	(DMSO)
		(18.6)
$PhSeCHPh_2$		(27.5)
$(PhSe)_2CH_2$		(31.3)
$PhSeCH_2Ph$		(31.0)
$PhSeCH{=}CHCH_2SePh$		(27.2)

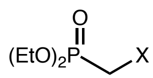
AMMONIUM

Substrate	pKa H_2O	(DMSO)
$Me_3N^+CH_2X$		
X= CN		(20.6)
SO_2Ph		(19.4)
COPh		(14.6)
CO_2Et		(20.0)
$CONEt_2$		(24.9)

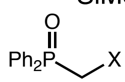
PHOSPHONIUM

Substrate	pKa H_2O	(DMSO)
P^+H_4	-14	
MeP^+H_3	2.7	
Et_3P^+H	9.1	
$Ph_3P^+CH_3$		(22.4)
Ph_3P^+*i*-Pr		(21.2)
$Ph_3P^+CH_2COPh$		(6.2)
$Ph_3P^+CH_2CN$		(7.0)

PHOSPONATES & PHOSPHINE OXIDES



Substrate	pKa H_2O	(DMSO)
X= Ph		(27.6)
CN		(16.4)
CO_2Et		(18.6)
Cl		(26.2)
$SiMe_3$		(28.8)



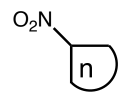
Substrate	pKa H_2O	(DMSO)
X= SPh		(24.9)
CN		(16.9)

PHOSPHINES

Substrate	pKa H_2O	(DMSO)
$Ph_2PCH_2PPh_2$		(29.9)
$Ph_2PCH_2SO_2Ph$		(20.2)

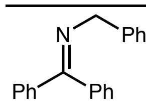
NITRO

Substrate	pKa H_2O	(DMSO)
RNO_2		
R= CH_3	≈10	(17.2)
CH_2Me		(16.7)
$CHMe_2$		(16.9)
CH_2Ph		(12.2)
CH_2Bn		(16.2)
CH_2SPh		(11.8)
CH_2SO_2Ph		(7.1)
CH_2COPh		(7.7)



Substrate	pKa H_2O	(DMSO)
n= 3		(26.9)
4		(17.8)
5		(16.0)
6		(17.9)
7		(15.8)

IMINES

Substrate	pKa H_2O	(DMSO)
		(24.3)

Oxime ethers are ~ 10 pka units less acidic than their ketone counterparts Streitwieser, JOC 1991, 56, 1989

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JOC 41, 2786 (1976)
JOC 41, 2508 (1976)
JOC 42, 1817 (1977)
JOC 42, 321 (1977)
JOC 42, 326 (1977)
JOC 43, 3113 (1978)
JOC 43, 3095 (1978)
JOC 43, 1764 (1978)
JOC 45, 3325 (1980)
JOC 45, 3305 (1980)
JOC 45, 3884 (1980)
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J. March (1985)
Unpublished results of W. P. Jencks

THF:
JACS 110, 5705 (1988)

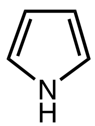
See cited website below for additional data

*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Brodwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

DMSO Acidities of Common Heterocycles

Bordwell, ACR, **1988**, *21*, 456
Bordwell http://www.chem.wisc.edu/areas/reich/pkatable/index.htm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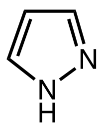
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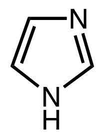
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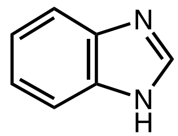
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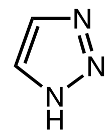
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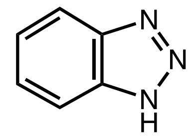
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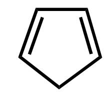
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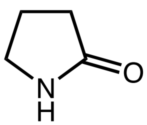
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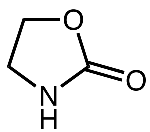
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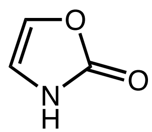
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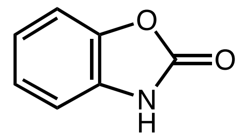
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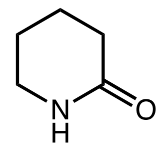
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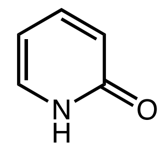
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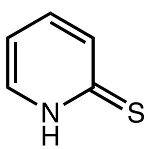
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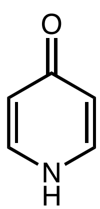
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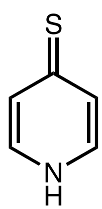
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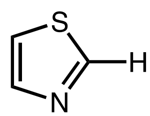
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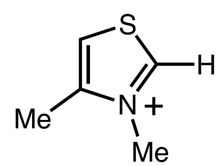
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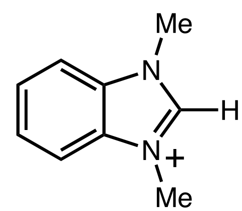
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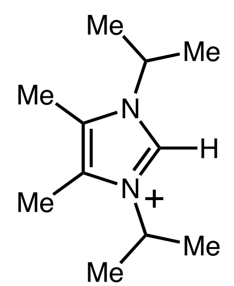
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