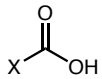
pKa's of Inorganic and Oxo-Acids

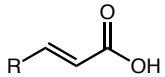
INORGANIC ACIDS

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	

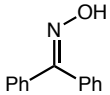


Substrate	pKa H_2O	(DMSO)
R= H	4.25	
trans-CO_2H	3.02, 4.38	
cis-CO_2H	1.92, 6.23	

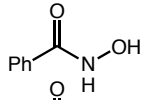
ALCOHOLS

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)

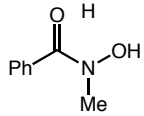
OXIMES & HYDROXAMIC ACIDS



Substrate	pKa H_2O	(DMSO)
	11.3	(20.1)



Substrate	pKa H_2O	(DMSO)
	8.88 (NH)	(13.7)

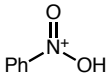


Substrate	pKa H_2O	(DMSO)
		(18.5)

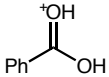
PEROXIDES

Substrate	pKa H_2O	(DMSO)
MeOOH	11.5	
CH_3CO_3H	8.2	

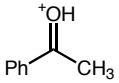
PROTONATED SPECIES



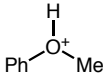
Substrate	pKa H_2O	(DMSO)
	-12.4	



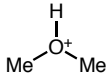
Substrate	pKa H_2O	(DMSO)
	-7.8	



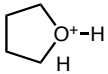
Substrate	pKa H_2O	(DMSO)
	-6.2	



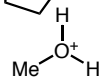
Substrate	pKa H_2O	(DMSO)
	-6.5	



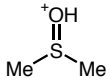
Substrate	pKa H_2O	(DMSO)
	-3.8	



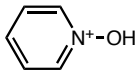
Substrate	pKa H_2O	(DMSO)
	-2.05	



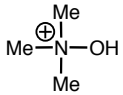
Substrate	pKa H_2O	(DMSO)
	-2.2	



Substrate	pKa H_2O	(DMSO)
	-1.8	

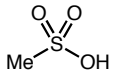


Substrate	pKa H_2O	(DMSO)
	0.79	(+1.63)

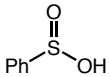


Substrate	pKa H_2O	(DMSO)
		(+5.55)

SULFINIC & SULFONIC ACIDS



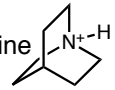
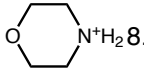
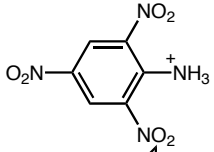
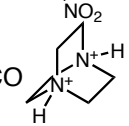
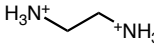
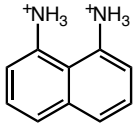
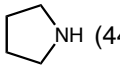
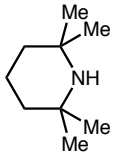
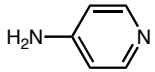
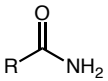
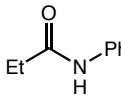
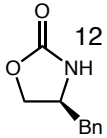
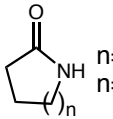
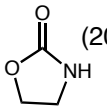
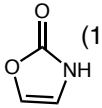
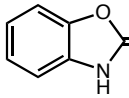
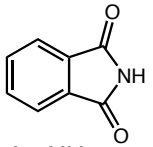
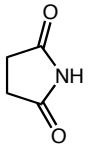
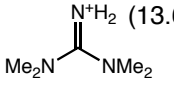
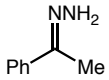
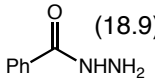
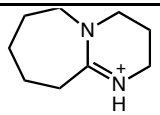
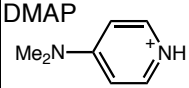
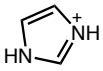
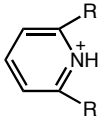
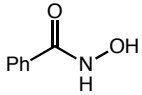
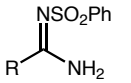
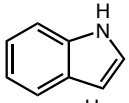
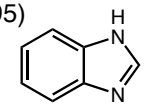
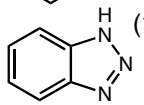
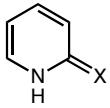
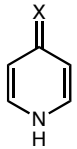
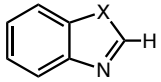
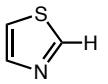
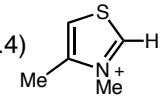
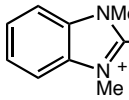
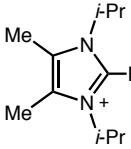
Substrate	pKa H_2O	(DMSO)
	-2.6	



Substrate	pKa H_2O	(DMSO)
	2.1	

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

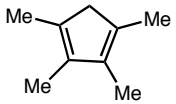
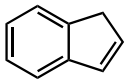
For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

Substrate	pKa H_2O	(DMSO)
PROTONATED NITROGEN		
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		
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= H	(23.5)
	CH_3 15.1	(25.5)
	Ph	(23.3)
	CF_3	(17.2)
	(urea) NH_2	(26.9)
	OEt	(24.8)
	(21.6)	
	12	(20.5)
	n= 1 (24.1) n= 2 (26.4)	
		(20.8)
	(15)	
		(12.1)
IMIDES		
	8.30	
		(14.7)
Ac_2NH		(17.9)
SULFONAMIDE		
RSO_2NH_2	R = Me	(17.5)
	Ph	(16.1)
	CF_3 6.3	(9.7)
$MeSO_2NHPh$		(12.9)
GUANIDINIUM, HYRDAZONES,- IDES, & -INES		
	(13.6)	
		(21.6)
	(18.9)	
$PhSO_2NHNH_2$		(17.2)
PhNHNHPh		(26.1)
PROTONATED HETEROCYCLES		
DBU 	(12) (estimate)	
DMAP 	9.2	
		6.95
	R= H (PPTS)	5.21 (3.4)
	t-Bu	4.95 (0.90)
	Me	6.75 (4.46)
	Cl, H	0.72
HYDROXAMIC ACID & AMIDINES		
	8.88 (NH)	(13.7)
	R= Me	(17.3)
	Ph	(15.0)
HETEROCYCLES		
	(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)

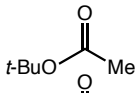
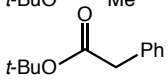
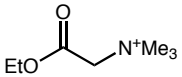
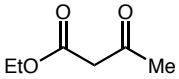
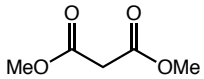
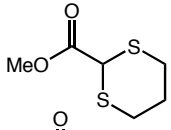
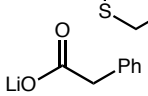
*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

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

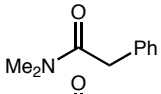
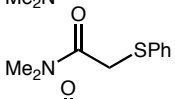
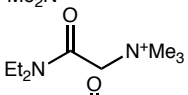
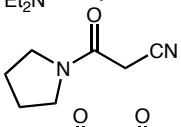
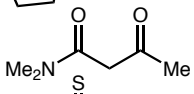
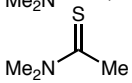
HYDROCARBONS

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	

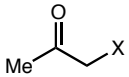
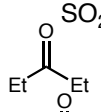
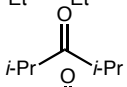
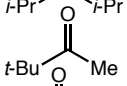
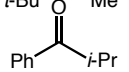
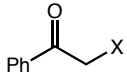
ESTERS

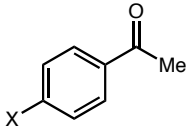
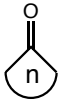
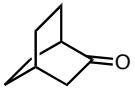
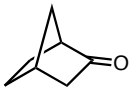
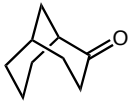
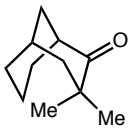
Substrate	pKa H_2O	(DMSO)
	24.5	(30.3)
		(23.6)
		(20.0)
	11	(14.2)
	13	(15.7)
		(20.9)
		[30.2 (THF)]

AMIDES

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

KETONES

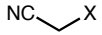
Substrate	pKa H_2O	(DMSO)
		
X= H		(26.5)
Ph		(19.8)
SPh		(18.7)
$COCH_3$	9	(13.3)
SO_2Ph		(12.5)
	19-20	(27.1)
		(28.3)
		(27.7)
		(26.3)
		
X= H		(24.7)
CH_3		(24.4)
Ph		(17.7)
$COCH_3$		(14.2)
COPh		(13.3)
CN		(10.2)
F		(21.6)
OMe		(22.85)
OPh		(21.1)
SPh		(16.9)
SePh		(18.6)
NPh_2		(20.3)
N^+Me_3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

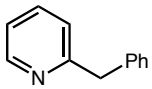
For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

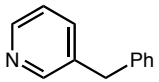
NITRILES

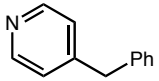


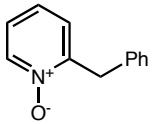
Substrate	pKa H_2O	(DMSO)
X= H		(31.3)
CH_3		(32.5)
Ph		(21.9)
COPh		(10.2)
$CONR_2$		(17.1)
CO_2Et		(13.1)
CN	11	(11.1)
OPh		(28.1)
N^+Me_3		(20.6)
SPh		(20.8)
SO_2Ph		(12.0)

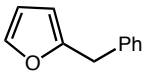
HETERO-AROMATICS


(28.2)


(30.1)


(26.7)


(25.2)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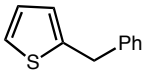
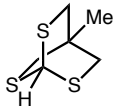

(30.0)

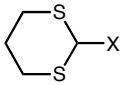
SULFIDES

$PhSCH_2X$

Substrate	pKa H_2O	(DMSO)
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)

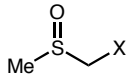

(30.5)

Substrate	pKa H_2O	(DMSO)
$(PhS)_2CHPh$		(23.0)

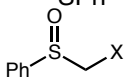


Substrate	pKa H_2O	(DMSO)
X= Ph		(30.7)
CO_2Me		(20.8)
CN		(19.1)
$RSCH_2CN$		
R= Me		(24.3)
Et		(24.0)
i-Pr		(23.6)
t-Bu		(22.9)
$PhSCH{=}CHCH_2SPh$		(26.3)
BuSH	10-11	(17.0)
PhSH	≈7	(10.3)

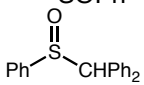
SULFOXIDES



Substrate	pKa H_2O	(DMSO)
X= H		(35.1)
Ph		(29.0)
SPh		(29.0)

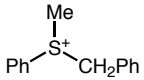


Substrate	pKa H_2O	(DMSO)
X= H		(33)
Ph		(27.2)
SOPh		(18.2)


(24.5)

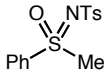
SULFONIUM

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)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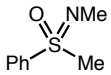
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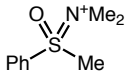
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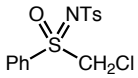
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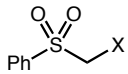
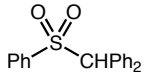
SULFONES



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)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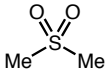
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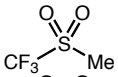
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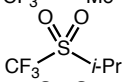
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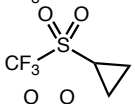
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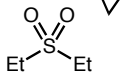
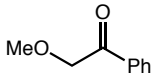
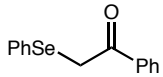
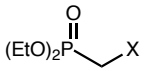
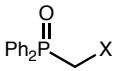

(32.8)

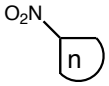
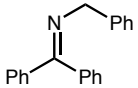
Substrate	pKa H_2O	(DMSO)
$(PhSO_2)_2CH_2Me$		(14.3)

*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

Substrate	pKa H_2O	(DMSO)
ETHERS		
CH_3OPh		(49)
$MeOCH_2SO_2Ph$		(30.7)
$PhOCH_2SO_2Ph$		(27.9)
$PhOCH_2CN$		(28.1)
		(22.85)
SELENIDES		
		(18.6)
$PhSeCHPh_2$		(27.5)
$(PhSe)_2CH_2$		(31.3)
$PhSeCH_2Ph$		(31.0)
$PhSeCH{=}CHCH_2SePh$		(27.2)
AMMONIUM		
$Me_3N^+CH_2X$		
X= CN		(20.6)
SO_2Ph		(19.4)
COPh		(14.6)
CO_2Et		(20.0)
$CONEt_2$		(24.9)

Substrate	pKa H_2O	(DMSO)
PHOSPHONIUM		
P^+H_4		-14
MeP^+H_3		2.7
Et_3P^+H		9.1
$Ph_3P^+CH_3$		(22.4)
$Ph_3P^+i\text{-}Pr$		(21.2)
$Ph_3P^+CH_2COPh$		(6.2)
$Ph_3P^+CH_2CN$		(7.0)
PHOSPONATES & PHOSPHINE OXIDES		
		
X= Ph		(27.6)
CN		(16.4)
CO_2Et		(18.6)
Cl		(26.2)
$SiMe_3$		(28.8)
		
X= SPh		(24.9)
CN		(16.9)
PHOSPHINES		
$Ph_2PCH_2PPh_2$		(29.9)
$Ph_2PCH_2SO_2Ph$		(20.2)

Substrate	pKa H_2O	(DMSO)
NITRO		
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)
		
n= 3		(26.9)
4		(17.8)
5		(16.0)
6		(17.9)
7		(15.8)
IMINES		
		(24.3)

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

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JACS 97, 7160 (1975)
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JACS 105, 6188 (1983)
JOC 41, 1883 (1976)
JOC 41, 1885 (1976)
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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Acc. Chem. Res. 21, 456 (1988)
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Advanced Org. Chem., 3rd Ed.
J. March (1985)
Unpublished results of W. P. Jencks

THF:
JACS 110, 5705 (1988)

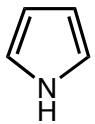
See cited website below for additional data

*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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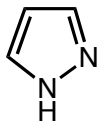

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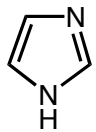

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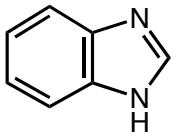

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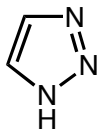

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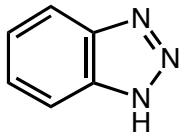

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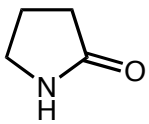

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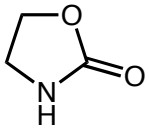

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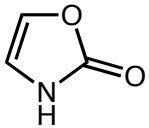

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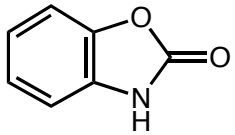

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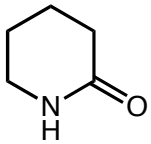

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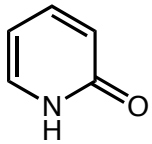

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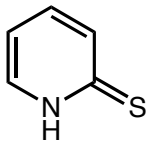

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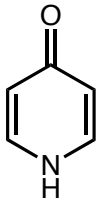

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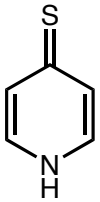

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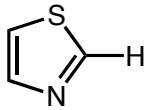

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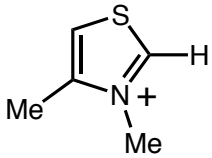

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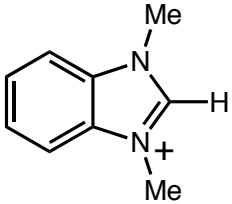

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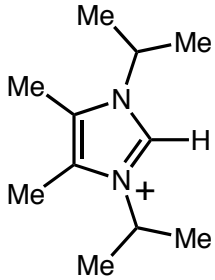

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