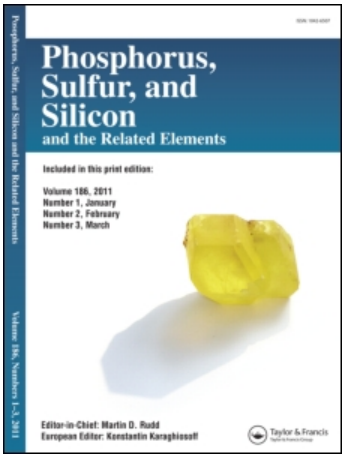

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OXIDATION PRODUCTS OF CYCLIC THIONES

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OXIDATION PRODUCTS OF CYCLIC THIONES

by

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CONTENTS

I. INTRODUCTION

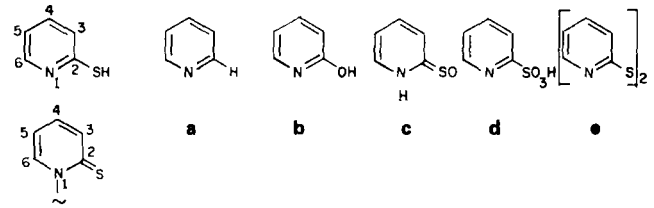
A large number of cyclic thiones has been synthesized. These include alicyclic and heterocyclic thiones, the latter including those with potential aromatic character. It is the intention of this paper to summarize the reactions of a number of simple systems of this type with a variety of reagents which lead to modification of the thione function. Reactions may either lead to oxidation of the molecule, replacement of the thione sulfur atom by oxygen, or even replacement by hydrogen. Data are also included for some thiols which are capable of tautomerism with thiones and give similar or related products.

II. TYPES OF THIONES OXIDIZED

These include alicyclic thiones with three to seven-membered rings, and are usually conjugated. Non-conjugated thiones correspond to aliphatic acyclic thiones and are likely to be polymeric.[1] Heterocyclic thiones described here have five- to seven-membered rings, and thione functions are stabilized by interaction with heteroatoms, including nitrogen, oxygen and sulfur, or by conjugation with double bonds. In some compounds, especially in nitrogen heterocycles, they may exist substantially as thiol forms. Heterocyclic thiones described also include those with two or more heteroatoms. Types of thiones oxidized are classified and appear with the appropriate reagents and types of products in Tables I to XXVII.

TABLE I

Oxidation Reactions of 2-Mercapto Pyridines or Pyrid-2-Thiones

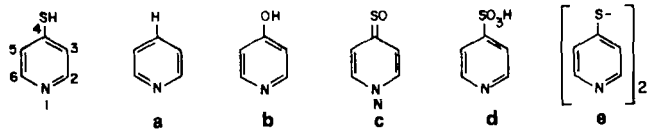


a b c d e

Derivative	Oxidizing agent	Product	Reference
Parent	HNO_3	d	145
parent	H_2O_2	c	7a
1-Me	H_2O_2	c	7a
5-Cl	10% H_2O_2	e	11
5-Br	10% H_2O_2	e	11
5-I	10% H_2O_2	e	11
5-NO_2	10% H_2O_2	e	11
5-NO_2	$KMnO_4$/acetone	b	18
5-NO_2	$KMnO_4/NH_4OH$	b	18
5-NO_2	CrO_3	b	18
5-NO_2	HNO_3	b	18
5-$NHCOCH_3$	H_2O_2	d	18
3-Cl-5-NO_2	10% H_2O_2	e	11
3-CN-4,6-Me_2	H_2O_2/NaOH	d	40
3-CN-4,6-Me_2	HNO_3	e	40
3-CN-4,6-Me_2	I_2/K_2CO_3	e	40
5,6-(−CH=CH−CMe=CH−)	I_2/KI	e	88
4-Me-5,6-(−CH=CH−CCl=CH−)	I_2/KI	e	88

TABLE II

Oxidation Reaction of 4-Mercaptopyridines

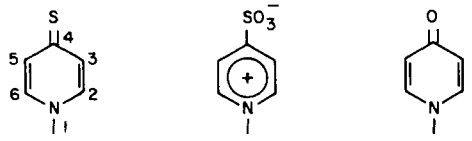


a b c d e

Derivative	Oxidizing agent	Product	Reference
Parent	HNO_3	d	92
Parent	HNO_3	d + e	39
Parent	Cl_2/HCl	d	39
Parent	Cl_2/ether	e	39
Parent	Cl_2/HNO_3	e	39
Parent	I_2/KI, NaOH	e	92
Parent	I_2/NaOH	e	39
Parent	$NaOCl/NH_4OH$, NaOH	e	39
Parent	H_2O_2/NH_4OH	e	39
Parent	H_2O_2	c	7
3,5-X_2, X=I, Br, Cl	H_2O_2	a	12
3,5-X_2, X=I, Br, Cl	HNO_3	b	12
	$KMnO_4$	d	12

TABLE III

Oxidation Reactions of Pyridine-4-Thiones

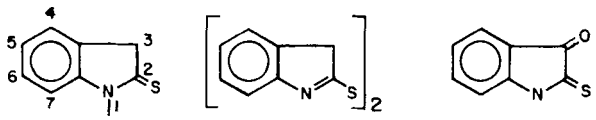


a b

Derivative	Oxidizing agent	Product	Reference
1,2,6-Me_3	H_2O_2/HOAc	a	50a
1-Et,-2,6-Me_2	H_2O_2/HOAc	a	50a
1-Me-2,6-Ph_2	H_2O_2/HOAc	a	50a
1-Et-2,6-Ph_2	H_2O_2/HOAc	a	50a
3,5-Br_2-1,2,6-Me_3	H_2O_2/HOAc	a	50b
3,5-Br_2-1-Et-2,6-Me_2	H_2O_2/HOAc	a	50b
3,5-Br_2-1-Me-2,6-Ph_2	H_2O_2/HOAc	a	50b
3,5-Br_2-1-Et-2,6-Ph_2	H_2O_2/HOAc	a	50b

TABLE IV

Oxidation Reactions of Indolinethiones



a b

Compound	Oxidizer	Product	Reference
Parent	O2/ether	a	2
1-Me	O_2/ether	a	2
3-Me	O_2/ether	a	2
3-Ph	O_2/ether	a	2
3-CH_2Ph	O_2/ether	a	2
3-t-Bu	O_2/ether	a	2
3-C_6H_4p-OMe	O_2/ether	a	2
1-Me-3-Ph	O_2/ether	a	2
1-Me	O_2/2 weeks	b	2
3,3,7-Me_3	$K_3Fe(CN)_6$	a	173
3,3,5-Me_3	$K_3Fe(CN)_6$	a	173

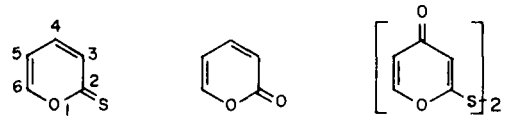
TABLE V

Oxidation of Miscellaneous Heterocycles Containing One Nitrogen Atom

Compound	Oxidizer	Product	Reference
Monothiosuccinimide	H_2O_2	Succinimide	7b
Dithiophthalimide	H_2O_2	Monothiophthalimide	7b
Monothiophthalimide	H_2O_2	Phthalimide	7b
Thiocaprolactone	H_2O_2	Thiocaprolactone S-oxide	7a

TABLE VI

Oxidation Reactions of Pyran-2-Thiones

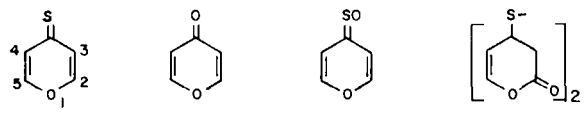


a b

Derivative	Oxidizing agent	Product type	Reference
4,6-Ph_2	H_2O_2/HOAc	a	52
5,6-$(CH{=}CH{-})_2$	H_2O_2/HOAc	a	52
	H_2O_2/KOH	a	46
3-Me-5,6-(CH−CMe−CH=CH−)	$Hg(OAc)_2$	a	97
4-OH-4,6-(−CH=CMe−CH=CH−)	Nitrous fumes	3-nitro "a"	89
	I_2/EtOH	b	89
3,4-$(CH{=}CH)_2$-6-Ph	$KMnO_4$	a	123
6-C_6H_5p·Br-5-OPh	Et_3N	a	149
6-C_6H_5p·Br-5-OC_6H_4p·Me	Et_3N	a	149
6-C_6H_4p·Ph-5-Ph	Et_3N	a	149
6-C_6H_4p·Ph-5-OC_6H_4p·Me	Et_3N	a	149
4,6-Ph_2-5-OPh	H_2O_2/HOAc	a	51
4,6-Ph_2-5-OC_6H_4p·Me	H_2O_2/HOAc	a	51
4,6-Ph_2-5-OC_6H_4p·Cl	H_2O_2/HOAc	a	51
4,6-Ph_2-5-OC_6H_4p·Br	H_2O_2/HOAc	a	51
4,5,6-Ph_3	H_2O_2/HOAc	a	51
4-Ph-5-OPh-6-O-C_6H_4p·Me	H_2O_2/HOAc	a	51

TABLE VII

Oxidation Reactions of Pyran-4-Thiones



a b c

Derivative	Oxidizing agent	Product type	Reference
Parent	O_2/hν	a	3
2,6-Me_2	O_2/hν	a	3
2,6-Me_2	H_2O_2/HOAc	a	4b, 52
2,6-Ph_2	O_2/hν	a	3
2,6-Ph_2	H_2O/HOAc	a	52, 4b
2,-C_6H_4p·OMe-6-Ph	H_2O_2/HOAc	a	4b
2,6-$(C_6H_4$p·OMe$)_2$	H_2O_2/HOAc	a	4b
	O_2	a	4b
5,6-$(CH{=}CH)_2$-2-Ph	H_2O_2/HOAc	a	52
2,3:5,6-$(CH{=}CH{-}CH{=}CH)_2$	$SOCl_2$	a	148
2,3:5,6-(CH=CH−CH=CH)	ClCO·COCl	a	148

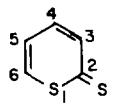
TABLE VII—continued

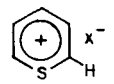
Oxidation Reactions of Pyran-4-Thiones

Derivative	Oxidizing agent	Product type	Reference
2,3:5,6-(CH=CH–CH=CH)	$HO_2C,C_6H_4 \cdot OCO_3H$	b	53
2,3:5,6-(CH=CH–CH=CH)	O_2	a	4
2-Ph-[1,2-b]-Naphtho	$KMnO_4$	a	129
2-C_6H_4o · OMe-[1,2-b]-Naphtho	$KMnO_4$	a	129
2-C_6H_4p · OMe-[1,2-b]-Naphtho	$KMnO_4$	a	129
2-C_6H_3(2,3-$(OMe)_2$)-[1,2-b]-Naphtho	$KMnO_4$	a	129
2-C_6H_3(3,4-$(OMe)_2$)-[1,2-b]-Naphtho	$KMnO_4$	a	129
2-C_6H_4p · Me-[1,2-b]-Naphtho	$KMnO_4$	a	129
2-(2-Furyl)-[1,2-b]-Naphtho	$KMnO_4$	a	129
2-(2-Thienyl)-[1,2-b]-Naphtho	$KMnO_4$	a	129

TABLE VIII

Oxidation Reactions of Thiopyran-2-Thiones





a

b

Derivative	Oxidizing agent	Product type	Reference
Parent	$HgCl_2$	b	93
3,6-Ph_2	H_2O_2/HOAc	a	52
3,5-Ph_2	H_2O_2/HOAc	a	160
4,6-Ph_2	H_2O_2/HOAc	a	52
4,6-Ph_2	HgOAc	b	96
3-COC_6H_4pOMe-6-C_6H_4p · OMe	$Hg(OAc)_2$	b	56
3-COC_6H_4pOMe-6-C_6H_4p · OMe	$KMnO_4$	b	56
5,6-$(CH=CH)_2$	$HgCl_2$	b	93
3,4-$(CH=CH)_2$-6-Ph	KM_2O_4	b	123
3,4-$(CH=CH)_2$-6-Ph	H_2O_2/HOAc	b	160
3,4-$(CH=CH)_2$-6-C_6H_4p · Me	$KMnO_4$	b	123
3,4-$(CH=CH)_2$-6-C_6H_4p · OMe	$KMnO_4$	b	123
3,4-$(CH=CH)_2$-6-C_6H_4p · Cl	$KMnO_4$	b	123
3,4-$(CH=CH)_2$-6-[–C_6H_3-2′,4′$(OMe)_2$]	$KMnO_4$	b	123
3,4-$(CH=CH)_2$-6-[C_6H_3-3′,4′-$(OMe)_2$]	$KMnO_4$	b	123
3,4$(CH=CH)_2$-6-[C_6H_3-2′,5′-$(OMe)_2$]	$KMnO_4$	b	123
3,4$(CH=CH)_2$-6-(C_6H_3-2′,4′-Me_2)	$KMnO_4$	b	123
3,4$(CH=CH)_2$-6-(C_6H_3′,4′-Me_2)	$KMnO_4$	b	123
3,4-$(CH=CH)_2$-6-(C_6H_3-2′,5′-Me_2)	$KMnO_4$	b	123
3,4-$(CH=CH)_2$-5,6-Ph_2	$KMnO_4$	b	123
5,6-$(CH=CH)_2$-3-Me	H_2O_2/HOAc	a, b	160
5,6-(CH=CH–CH=CMe)-3-Me	H_2O_2/HOAc	b	160
5,6-(CH–COMe–CH=CH)	H_2O_2/HOAc	b	160
3,4:5,6-$(CH=CH–CH=CH)_2$	H_2O_2/HOAc	b	160

TABLE IX

Oxidation Reactions of Thiopyran-4-Thiones

a

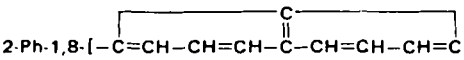
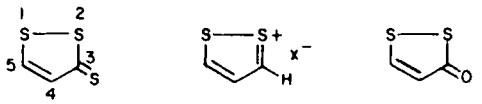
Derivative	Oxidizing agent	Product type	Reference
Parent	$O_2/h\nu$	a	3
	$HgCl_2$	a	93
2,6-Me_2	$O_2/h\nu$	a	3
	$KMnO_4$	a	124
2-Ph	$HgCl_2$	a	94
2,6-Ph_2	$O_2/h\nu$	a	3
2,6-Ph_2	$HgCl_2$	a	95
2,6-Ph_2	H_2O_2/HOAc	a	52
2,6-$(SMe)_2$-3,5-Ph_2	$SOCl_2$	a	148
2,6-$(SMe)_2$-3,5-Ph_2	Cl·COCOCl	a	148
2,6-$(SEt)_2$-3,5-Ph_2	$SOCl_2$	a	148
	CCl·COCOCl	a	148
2,6-$(CH{=}CH)_2$	$HgCl_2$	a	93
2-Ph-5,6-$(CH{=}CH)_2$	$SOCl_2$	a	148
2-Ph-5,6-$(CH{=}CH)_2$	Cl·CO·COCl	a	148
2-Ph-5,6-$(CH{=}CH)_2$	H_2O_2/HOAc	a	52
2,3:5,6-$(CH{=}CH{-}CH{=}CH)_2$	$O_2/h\nu$	a	4
	$HO_2C\cdot C_6H_4OCO_3H$	a	53
	$KMnO_4$	a	122

TABLE X

Oxidation Reactions of 1,2-Dithiole-3-Thiones



a b

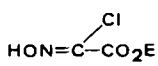
Derivative	Oxidizing agent	Product type	Reference
Parent	H_2O_2/HOAc	a	57
Parent	$KMnO_4$	b	120
Parent	$Hg(OAc)_2$	b	98
4-Me	$Hg(OAc)_2$	b	99
4-Et	$Hg(OAc)_2$	b	99
4,5-Me_2	H_2O_2/HOAc	a	63
5-tC_5H_{11}	Cl_2/H_2O	b	85
4-$(Me)_3C$-5-Me	Cl_2/H_2O	b	85
5-CO_2H	$CH_3\cdot CO_3H$	5-H-a	58a
4-Ph	$CH_3\cdot CO_3H$	a	56, 58b
4-Ph	$Cl_3C{-}N{=}CCl_2$	b	150
4-Ph	$CSCl_2$	b	150
4-Ph		b	151

TABLE X—*continued*

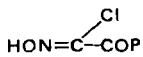
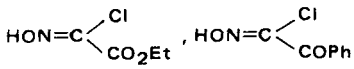
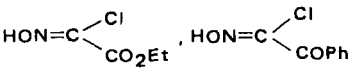
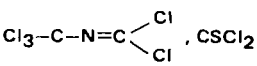
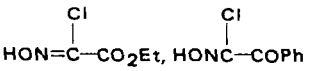
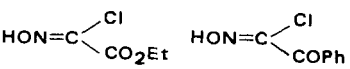
Derivative	Oxidizing agent	Product type	Reference
4-Ph		b	151
5-Ph	$CH_3 \cdot CO_3H$	a	56, 58b
5-Ph	H_2O_2/HOAc	a	59
5-Ph	D_2O_2/DOAc	3-D-a	64
5-Ph	H_2O_2	Ph–CH_2OH	14
5-Ph	HNO_3	$PhCH_2OH$	14
5-Ph	$KMnO_4$	b	14, 126
5-Ph	$Cl_3C–N=CCl_2$ or $CSCl_2$	b	150
5-Ph		b	151
5-Ph	Cl_2/HOAc, H_2O	b, 4-Cl-b	79
5-Ph	Br_2	b, 4-Br-b	79
4,5-Ph_2	$CH_3 \cdot CO_3H$	a	56
4,5-Ph_2	$Cl_3CN=CCl_2$, $CSCl_2$	b	150
4,5-Ph_2		b	151
5-$C_6H_4p \cdot Cl$	$CH_3 \cdot CO_3H$	a	56
5-$C_6H_4p \cdot Cl$	Cl_2	4-Cl–B	79
5-$C_6H_4p \cdot Cl$	Br_2	4-Br-b	79
5-$C_6H_4p \cdot Cl$		b	150
5-$C_6H_4p \cdot Cl$		b	151
5-$C_6H_4p \cdot Br$	Cl_2	b + 4-Cl-b	79
5-$C_6H_4p \cdot Br$	Br_2	4-Br-b	79
5-$C_6H_4p \cdot Br$	$Cl_3–C=N=CCl_2$, $CSCl_2$	b	150
5-$C_6H_4p \cdot Br$		b	151
5-(2-Thienyl)	$CH_3 \cdot CO_3H$	a	56
5-(C_6H_3-3′,4′-$(OMe)_2$)	$KMnO_4$	b	120
5-(C_6H_3-3′-Cl-4′-OMe)	$KMnO_4$	b	79
5-(C_6H_3-3′-Cl-4′-OMe)	Cl_2	b, 4-Cl-b	79
4-Br-5-Ph	$Cl_3C–N=CCl_2$, $CSCl_2$	b	150
4-D-5-Ph	H_2O_2/HOAc	a	62
4-Me-5-Ph	H_2O_2/HOAc	a	59
5-$pC_6H_4p \cdot Me$	$CH_3 \cdot CO_3H$	a	56
	$Cl_3CH=CCl_2$, or $CSCl_2$	b	150
		b	151
5-C_6H_4p ·OMe	Cl_2/HOAc	a, b	79
	$KMnO_2$	b	121, 126
	$CH_3 \cdot CO_3H$	a	56
	Br_2	b and 4-Brb	79
	CrO_3	$MeOC_6H_4pCO_2H$	137

TABLE X—*continued*

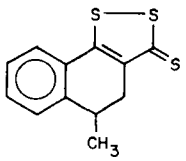
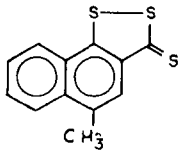
Derivative	Oxidizing agent	Product type	Reference
	$Cl_3CN{=}CCl_2$, $CSCl_2$	b	150
	$HON{=}C{=}CO_2Et$, $HON{=}C(Cl){-}COPh$	b	151
	a		
4-Ph-5-CO_2Et	$Hg(OAc)_2$	b	100b
4-CO_2Et-5-Ph	$Hg(OAc)_2$	b	100a
4-CO_2Et-5-C_6H_4p·OMe	$Hg(OAc)_2$	b	100a
4-CO_2Et-5-C_6H_4p·Cl	$Hg(OAc)_2$	b	100a
4-CO_2Et-5-(2-thienyl)	$Hg(OAc)_2$	b	100a
4-CN-5-Ph	$Hg(OAc)_2$	b	100a
4-CN-5-C_6H_4p·OMe	$Hg(OAc)_2$	b	100a
4-CN-5-C_6H_4p·Cl	$Hg(OAc)_2$	b	100a
4-CN-5-(2-Thienyl)	$Hg(OAc)_2$	b	100a
4-Cl-5-Ph	$Hg(OAc)$	b	100a
4-Cl-5-C_6H_4p·OMe	$Hg(OAc)_2$	b	100a
4-Cl-5-C_6H_4p·Cl	$Hg(OAc)_2$	b	100a
4-Cl-5-(2-Thienyl)	$Hg(OAc)_2$	b	100a
4,5-Ph_2	H_2O_2/HOAc	a	56, 59
5-SMe-4-Ph	$CH_3{\cdot}CO_3H$	a	61
5-SMe-4-Ph	$Hg(OAc)_2$	b	61
5-SMe-4-C_6H_4p·Me	$Hg(OAc)_2$	b	61
5-SMe-4-C_6H_4p·$C(CH_3)_3$	$Hg(OAc)_2$	b	61
5-Sme-4-C_6H_4p·$C(CH_3)_2{-}CH_2{-}CH_3$	$Hg(OAc)_2$	b	61
5-SMe-4-C_6H_4–p·Cl	$Hg(OAc)_2$	b	61
5-SMe-4-C_6H_4p·NO_2	$Hg(OAc)_2$	b	61
4, 5(–CH=CH)$_2$	$Cl_3CN{=}CCl_2$, $CSCl_2$	b	150
	$HON{=}C(Cl)CO_2Et$, $HON{=}C(Cl)COPh$	b	151
4,5-$(CH_2)_3$–	$HON{=}C(Cl)CO_2Et$, $HON{=}C(Cl)COPh$	b	151
O			
2,5-$CH_2CMe_2{-}CH_2{-}C$–	$KMnO_4$	b	102
	$Hg(OAc)_2$	b	102
2,5-$C(PhCH_2)_2{-}COCH_2{-}CMe_2$–	$Hg(OAc)_2$	b	102
	$CH_3{-}CO_3H$	a	71
	$CH_3{\cdot}CO_3H$	a	71
	$Hg(OAc)_2$	b	71

TABLE XI

Oxidation Reactions of Miscellaneous O, O; O, S, and S, S Heterocycles

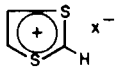
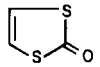
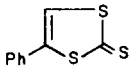
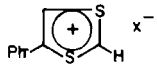
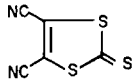
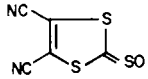
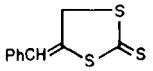
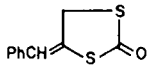
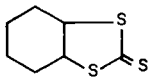
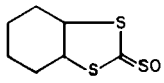
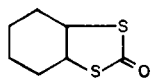
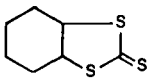
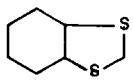
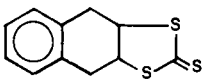
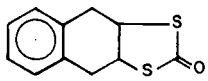
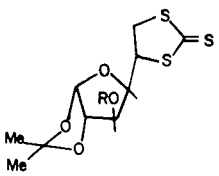
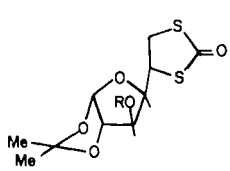
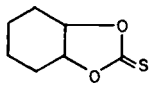
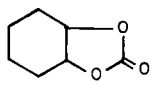
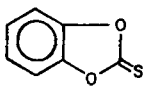
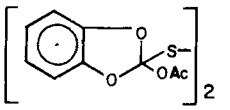
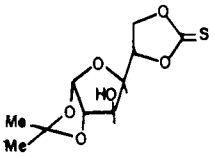
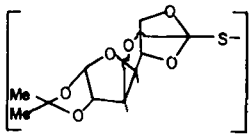
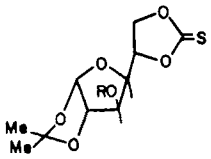
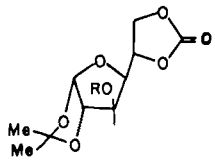
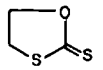
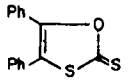
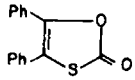
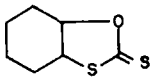
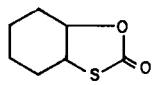
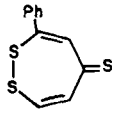
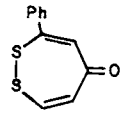
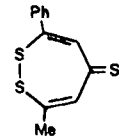
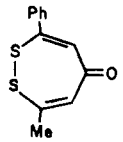
Compound	Oxidizing agent	Product	Reference
	CH_3-CO_3H		67
	CH_3-CO_2H/H_2O_2		57
	$Hg(OAc)_2$		98
	CH_3, CO_2H, H_2O_2		57
	CH_3-CO_3H		66
	HNO_3		147
	$Hg(OAc)_2$		110
	$Pb(OAc)_4$		65
"	CH_3-CO_3H		155
"	$Hg(OAc)_2$		65
	$KMnO_4$		155
	$Pb(OAc)_4$		155
	CH_3-CO_3H		155
	$Pb(OAc)_4$		139
	$Pb(OAc)_4$		155

TABLE XI—*continued*

Compound	Oxidizing agent	Product		Reference
	$Pb(OAc)_4$			155
	$Pb(OAc)_4$			139
	$Pb(OAc)_4$ $AgNO_3$			139
	60% HNO_3			140
	H_2O_2, CH_3CO_2H			160
	$Pb(OAc)_4$			155
	H_2SO_4		*	162
	H_2SO_4		*	162

* Suggested starting materials and products have wrongly assigned structures.

TABLE XII
Oxidation Reactions of Miscellaneous O, N Heterocyclic Thiones

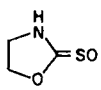
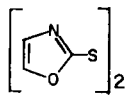
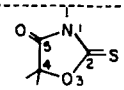
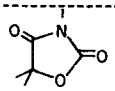
Compound	Oxidizing agent	Product	Reference
	H_2O_2		25
	I_2		90
			
4,4-Me_2	Cl_2/H_2O		84
1,4-Me_2-5-Et	Cl_2/H_2O		84
1-Et,4,4-Me_2	Cl_2/H_2O		84
1,4,4-Me_3	Cl_2/H_2O		84
1,4,4-Me_3	Br_2/H_2O		84

TABLE XII—*continued*

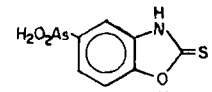
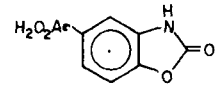
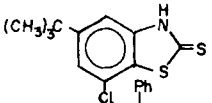
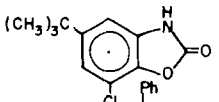
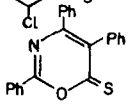
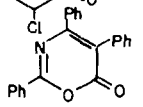
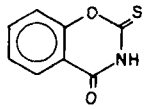
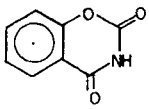
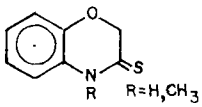
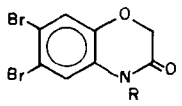
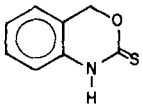
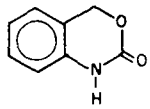
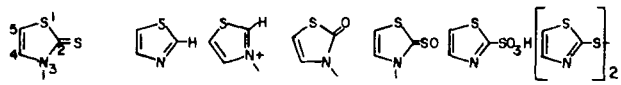
Compound	Oxidizing agent	Product	Reference
1,4,4-Me_3	$KMnO_4$		84
	$I_2/NaHCO_3$		74
	30% H_2O_2/HOAc		49
	$CH_3—CO_3H$		60
	H_2O_2		28
	Br_2		87
	H_2O_2/OH^-		27

TABLE XIII

Oxidation Reactions of Thiazoline-2-Thiones

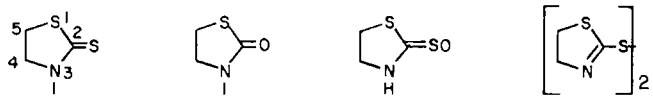


a_1 a_2 b c d e

Derivative	*Oxidizing agent*	Product type	Reference
Parent	Ethylene Oxide	b	158
Parent	I_2	e	90
4-Me	H_2O_2, neutral	a_1	20
	H_2O_2/OH^-	d	20
4-CO_2Et	H_2O_2/H^+	a_1	30
5-Me	Ethylene oxide	b	158
4,5-Me_2	H_2O_2	e + a_1	22
4,5-Me_2	H_2O_2/H^+	a_1	31, 32
3-Ph	$Hg(OAc)_2$	b	103
3-C_6H_4p · Me	$Hg(OAc)_2$	b	103
3-C_6H_4oMe	$Hg(OAc)_2$	b	103
3-C_6H_4p · OMe	$Hg(OAc)_2$	b	103
3-C_6H_4o · OMe	$Hg(OAc)_2$	b	103
3-Me-4-Ph	H_2O_2/HOAc	a_2	160
3-Et-4-Ph	H_2O_2/OH^-	b	47
5-CO_2H-4-Me	H_2O_2/H^+	a_1	30
5-CO_2Et-4-Me	H_2O_2/H^+	a_1	30
3-CH_2 pyrimidyl-4-Me-5-CH_2—CH_2OH	H_2O_2/HCl	a_1	38
3-CH_2 pyrimidyl-4-Me-5-CH_2—CH_2OH	H_2O_2, pH7,8,78	b	16
3-CH_2 pyrimidyl-4-Me-5-CH_2OAc	H_2O_2/HOAc	a_1	48

TABLE XIV

Oxidation Reactions of Thiazolidine-2-Thiones

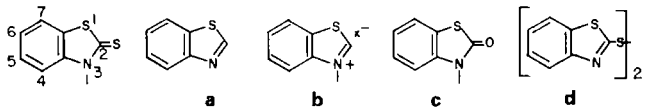


a b c

Derivative	Oxidizing agent	Product type	Reference
Parent	H_2O_2	b	79
	H_2O_2	c	19
4-O	H_2O_2	b	7a, 7b
5,5-Me_2	H_2O_2	c	21
3-Ph,–4–O–5–$(CH_3)_2C$=	$Hg(OAc)_2$	a	104

TABLE XV

Oxidation Reactions of Benzothiazoline-2-Thiones

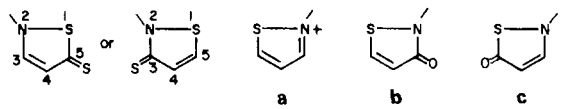


a b c d

Derivative	Oxidizing agent	Product type	Reference
Parent	H_2O_2/H^+	a	33
	H_2O_2/OH^-	c	41
	$2H_2O_2/OH^-$	a	42
	$4H_2O_2/OH^-$	c	2
	Cl_2/HCl	a	33
3-Me	H_2O_2/HOAc	b	160
Alkyl, amino and nitro derivatives	H_2O_2	d	13
5-NMe_2	H_2O_2/H^+	e	34
	H_2O_2/ethanol	e	34

TABLE XVI

Oxidation Reactions of Isothiazoline-3-and-5-Thiones and Benzisothiazoline-3-and-5-Thiones



a b c

Derivative	Oxidizing agent	Product type	Reference
2-Me–5-Ph–3-S	H_2O_2/HOAc	a	70a
2-Me–4,5Ph_2-3-S	H_2O_2/HOAc	a	70a
2,5-Ph_2-3-S	H_2O_2/HOAc	a	160
1-CH_2Ph-5-C_6H_4p · OMe	Ph N=C=O	b	156
2,4-Ph_2-5-S	H_2O_2/HOAc	a	69
2,3-Ph_2-5-S	H_2O_2/HOAc	a	69
2-Me-4-Ph-5-S	H_2O_2/HOAc	a	160

TABLE XVI—*continued*

Derivative	Oxidizing agent	Product type	Reference
2-CH_2Ph-4-Ph-5-S	H_2O_2/HOAc	a	160
2-Me-4,5-(CH=CH)$_2$-3-S	H_2O_2/HOAc	a	160
2-Me-3,4-(CH=CH)$_2$-5-S	H_2O_2/HOAc	a	160
2-Ph-3,4-(CH=CH)$_2$-5-S	$KMnO_4$	c	134
2-Ph-3,4-(CH=CH)$_2$-5-S	H_2O_2/HOAc	a	160
2-C_6H_4p · Me-3,4(CH=CH)$_2$-5-S	$KMnO_4$, CuO	c	134
2-C_6H_4p · OMe-3,4(CH=CH)$_2$-5-S	$KMnO_4$	c	134
2-C_6H_4p · Cl-3,4-(CH=CH)$_2$-5-S	$KMnO_4$	c	134
2-Ph-3,4-(CH=CCl–CH=CH)-5-S	$KMnO_4$	c	134
2-C_6H_4p · CH_3–3,4-(CH=CCl–CH=CH)-5-S	CuO	c	134

TABLE XVII

Oxidation Reactions of Miscellaneous N, S-Heterocyclic Thiones

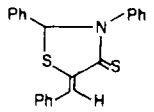
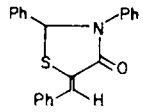
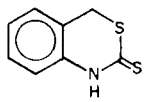
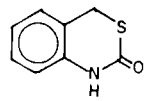
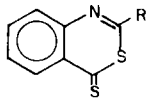
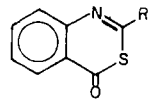
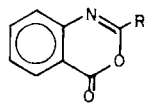
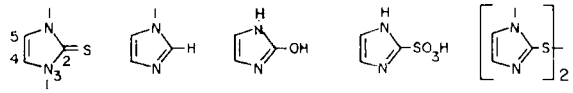
Compound	Oxidizing agent	Product	Reference
	30% H_2O_2		17
	H_2O_2/OH^-		27
	$KMnO_4$		105
	$Hg(OAc)_2$		105
	NaOH		105

TABLE XVIII

Oxidation Reactions of Imidazoline-2-Thiones



a **b** **c** **d**

Derivative	Oxidizing agent	Product type	Reference
Parent	HNO_3	b	146, a, b
4,5-dihydro	I_2	d, HI, 2I_2	83
4-Me	I_2	d, HI, 2I_2	83

TABLE XVIII—*continued*

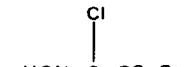
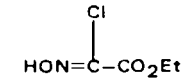
Derivative	Oxidizing agent	Product type	Reference
4-Me,4,5-dihydro	I_2	d, HI, $2I_2$	83
4-CH_2NH_2	HNO_3	4-CH_2OH-a	142
4-CH_2–NH–CS–NH_2	HNO_3	4-CH_2OH-a	142
1,3-Me_2	Pt electrode	b	152
4-C_6H_4p · Cl	HNO_3	a	143
4-(C_6H_3-3',4'$(OMe)_2$)	H_2PtCl_6	a	112
	HNO_3	a	112
	$EtNO_2$	a	112
4-(C_6H_2-2'-Me-3',4'-$(OMe)_2$)	H_2PtCl_6	a	112
4-Me-5-Ph	HNO_3	a	138
4-Me-5-CH_2Ph	HNO_3	a	141
4-5-Ph_2	HNO_3	a	119, 127
	$KMnO_4$	c	119, 127
		b	153
		b	153
4,5-$(CH=CH)_2$	I_2	d	91
4,5-$(CH=CH)_2$	$KMnO_4$	c	91
4,5-$(CH=CH)_2$	$AuCl_3$	a	113
4,5-(CH=CH(AsO_3H_2)CH=CH)	I_2/Na_2CO_3	a	74
4,5-(CH=CH($A_5O_3H_2$)CH=CH)	I_2	d · HI	91
4,5-(CH=CH($A_5O_3H_2$)CH=CH)	$KMnO_4$	c	91
4,5-(CH=CH(AsO_3H_2)CH=CH)	$AuCl_3$	a	113

TABLE XIX

Oxidation Reactions of Imidazolinethiones

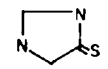
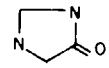
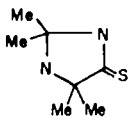
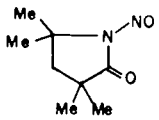
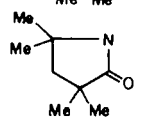
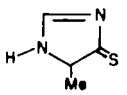
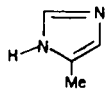
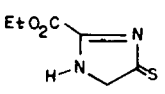
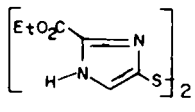
Compound	Oxidizing agent	Product	Reference
	$KMnO_4$		136
	HNO_3		43
	H_2O_2,OH^-		43
	HNO_3		75
	I_2,Na_2CO_3		75

TABLE XIX—*continued*

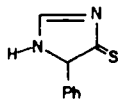
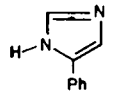
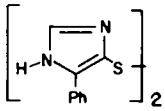
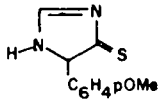
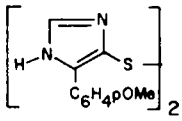
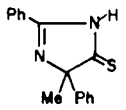
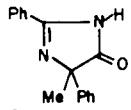
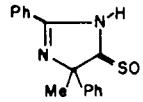
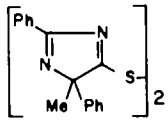
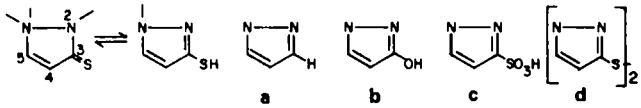
Compound	Oxidizing agent	Product	Reference
	HNO_3		75
"	O_2		5
	H_2O_2		5
	$I_2/KI,OH^-$		
	H_2O_2/OH^-		24
"	H_2O_2/MeOH		24
"	I_2,$NaHCO_3$		24

TABLE XX

Oxidation Reactions of Pyrazolinethiones



a b c d

Derivative	Oxidizing agent	Product	Reference
5-Me-2-Ph	I_2	d	8
5-Me-2-Ph	$KMnO_4$	d	8
5-Me-2-C_6H_4p · Me	HNO_2	d	8
5-Me-2-C_6H_4p · Me	$FeCl_3$	b	8
5-Me-2-C_6H_4p · Me	H_2O_2/OH^-	c	8
1,5-Me_2-2-Ph	H_2O_2	c	23
1,5-Me_2-2-Ph	H_2O_2/OH^-	b	23
1,2-Me_2-5-Ph	Cl_2/HOAc	c	80
4-PhCO-5-Me-2-Ph	H_2O_2	c	8
	I_2,KI	d	8

TABLE XXI

Oxidation Reactions of Miscellaneous Heterocyclic Thiones Containing Two Nitrogen Atoms

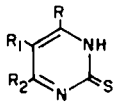
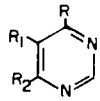
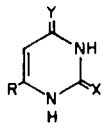
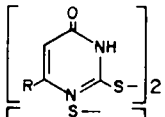
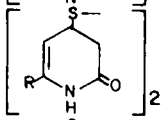
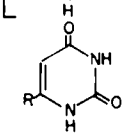
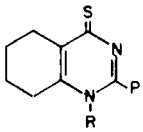
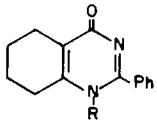
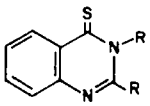
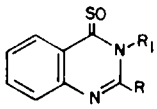
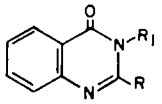
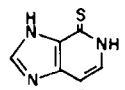
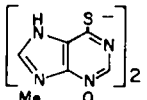
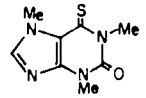
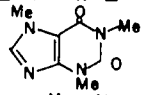
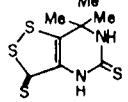
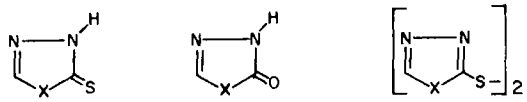
Compound	Substituents	Oxidizing agent	Product type	Reference
	R=R$_1$=R$_2$=H	H_2O_2/NaOH,HCl		36
	R=R$_2$=NH$_2$,R=H	H_2O_2/NaOH,HCl		37
	R$_1$=R$_1$=R$_2$=NH$_2$	H_2O_2/NaOH,HCl		37
	X=S,Y=O,R=H	I_2		90
	X=O,Y=S,R=H	I_2		90
	X=S,Y=O,R=CH$_3$	H_2O_2		27
	R=Ph	$Hg(OAc)_2$		106
	R=C$_6$H$_4$p·CF$_3$	$Hg(OAc)_2$		106
	R=C$_6$H$_4$p·F	$Hg(OAc)_2$		106
	R=R$_1$=H	H_2O_2		25
	R=Me,R$_1$=H	H_2O_2		25
	R=(Me)$_2$CH,R$_1$=H	H_2O_2		25
	R=(Me)$_3$C,R$_1$=H	H_2O_2		25
	R=(Me)$_3$CCH$_2$,R$_1$=H	H_2O_2		25
	R=Ph,R'=Me	$Hg(OAc)_2$		101
	R=Bu,R'=Ph	$Hg(OAc)_2$		101
		H_2O_2		7a
		H_2O_2/HOAc		7a
		$Hg(OAc)_2$		111

TABLE XXII

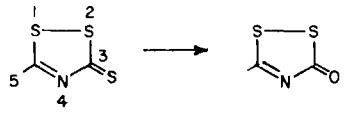
Oxidation Reactions of 4,1,2-Oxadiazoline-3-Thiones and 4,1,2-Thiadiazoline-3-Thiones



Derivative	Oxidizing agent	Product	Reference
X=O, 5-Me	HON=CCl–CO_2Et	a	153
X=O, 5-Ph	I_2/OH^-	b	76
X=O, 5-C_6H_4m · CH_3	I_2/OH^-	b	76
X=O,-5-(4-Pyridyl)	H_2O_2/OH^-	a	44
X=S, 5-NH_2	$FeCl_3$	b	9
	H_2O_2	b	9
	I_2	b	9
X=S,1,5-dihydro-5-Ph	I_2/OH^-	b	76
X=S, 5-NH–C_6H_4p · CH_3	I_2	b	77
X=S, 5-Ph–NH–NH	$FeCl_3$	b	116

TABLE XXIII

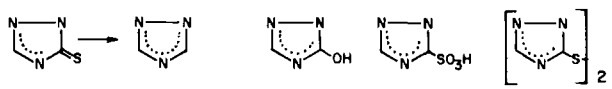
Oxidation Reactions of 1,2,4-Dithiazoline-3-Thiones



Derivative	Oxidizing agent	Reference
5-Ph	H_2O_2/HOAc	68
	$Hg(OAc)_2$	7a, 108
5-C_6H_4p · Br	$Hg(OAc)_2$	108
5-C_6H_4p · Cl	$Hg(OAc)_2$	108
5-C_6H_2o · Cl	$Hg(OAc)_2$	108
5-C_6H_3-2′-2′-Cl_2	$Hg(OAc)_2$	108
5-C_6H_4p · Me	H_2O_2/HOAc	159
5-C_6H_4p · OMe	$Hg(OAc)_2$	108
5-C_6H_4p · NO_2	$Hg(OAc)_2$	108
5-(2′thienyl)	$Hg(OAc)_2$	108

TABLE XXIV

Oxidation Reactions of 1,2,4-Triazolinethiones



a *b* *c* *d*

Derivative	Oxidizing agent	Product	Reference
Parent	O_3,HCl	d	6
	Cl_2	a, c	6
	Br_2	a	6
1-Ph	ethylene oxide, AcOH	2-CH_2–CH_2OH-b	157
4-Ph	ethylene oxide AcOH	2-CH_2–CH_2OH-b	157
5-NHPh	$FeCl_3$	d	115

TABLE XXIV—*continued*

Derivative	Oxidizing agent	Product	Reference
5-O	I_2	d	81
	$FeCl_3,H^+$	d	81
5-N=CH−Ph	H_2O_2	d	10
5-N(H)−N=CH−Ph	I_2	d	82
2-Me-4-Ph	ethylene oxide	b	158
5-NHPh-4-Ph	H_2O_2	d	10
	$FeCl_3$	d	10
H_2SO_4	H_2SO_4	d	10
1,2-Ph_2	I_2	d	86
1-(C_6H_4o · OH)-2-Ph	I_2	d	86
1-(C_6H_4p · Cl)-2-Ph	I_2	d	86
1-(C_6H_3-2′-Cl-4′-NO_2)-2-Ph	I_2	d	86
4-(C_6H_4p · CH_3)-5-S	I_2/OH^-	d	78
4-(C_6H_4o · CH_3)-5-S	I_2/OH^-	d	78
1,2,5-Ph_3	dioxane at 160°	b	154

TABLE XXV

Oxidation Reactions of Miscellaneous Heterocyclic Thiones Containing Three and Four Nitrogen Atoms

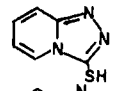
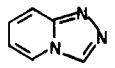
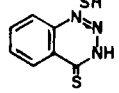
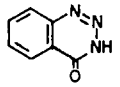
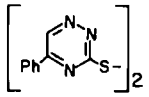
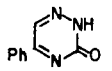
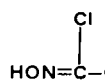
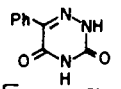
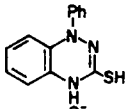
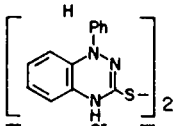
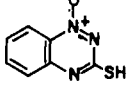
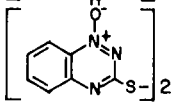
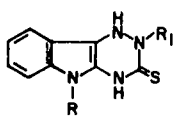
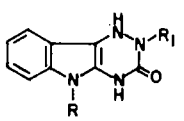
Compound	Oxidizing agent	Product	Reference
	dil · HNO_3		144
	$KMnO_4$		118
	I_2		45
	55% H_2O_2/NH_3		45
			153
	$FeCl_3$		116
	$NH_3,K_3Fe(CN)_6$		114
			

TABLE XXV—*continued*

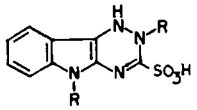
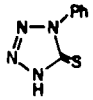
Compound	Oxidizing agent	Product	Reference
R=Me, R_1=H	$KMnO_4/OH^-$		125
R=H, R_1=Me	$KMnO_4/OH^-$		125
R=R_1=Me	$KMnO_4/OH^-$		125
R=R_1=H	$KMnO_4/OH^-$		125
	$KMnO_4/OH^-$		157

TABLE XXVI

Oxidation Reactions of Alicyclic Thiones

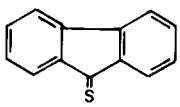
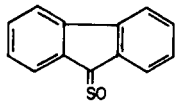
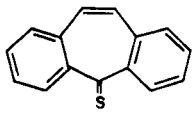
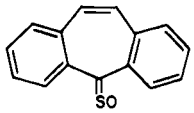
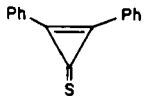
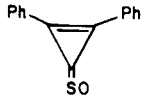
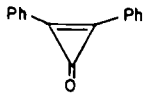
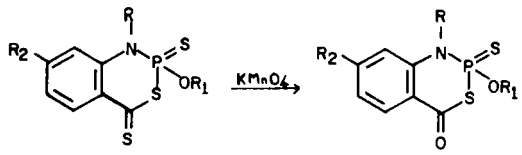
Compound	Oxidizing Agent	Product	Reference
	$HO_2C-C_6H_4oCO_3H$		53
	$HO_2C-C_6H_4oCO_3H$		55
	$HO_2C-C_6H_4oCO_3H$		72
"	$Pb(OAc)_4$		72
"	$Cl-C_6H_4mCO_3H$	"	72

TABLE XXVII

Oxidation Reactions of Thiaphosphazinethiones



Derivative			Reference
R	R_1	R_2	135
Ph	Me	H	135
Ph	Me	Cl	135
Ph	Et	H	135
Ph	Et	Cl	135

TABLE XXVII—*continued*

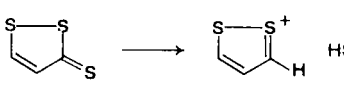
Derivative			Reference
$C_6H_4m \cdot CH_3$	Me	H	135
$C_6H_4m \cdot CH_3$	Et	H	135
$C_6H_4p \cdot$ Me	Me	H	135
$C_6H_4p \cdot$ Me	Me	Cl	135
$C_6H_4p \cdot$ Me	Et	H	135
$C_6H_4p \cdot$ Me	Et	Cl	135
$C_6H_4o \cdot$ OMe	Me	H	135
$C_6H_4o \cdot$ OMe	Me	Cl	135
$C_6H_4o \cdot$ OMe	Et	H	135
$C_6H_4p \cdot$ OMe	Me	H	135
$C_6H_4p \cdot$ OMe	Me	Cl	135
$C_6H_5p \cdot$ OMe	Et	H	135
$C_6H_4p \cdot$ OMe	Et	Cl	135
$C_6H_4m \cdot$ Cl	Me	H	135
$C_6H_4p \cdot$ Cl	Et	H	135
2-Naphthyl	Me	Cl	135
2-Naphthyl	Et	H	135
2-Naphthyl	Et	Cl	135

III. OXIDIZING AGENTS USED

There appears to be little limitation on which oxidizing agents may be employed. Even molecular oxygen is effective, sometimes under light-catalyzed conditions.[2-5] Ozone has also been used.[6] Reagents commonly used include hydrogen peroxide alone or at pH 7,[7-29] in acidic medium[30-38] or alkaline medium[8,16,20,23,27,36-43] or in combination as peracids.[7,44-73] Three halogens, chlorine, bromine, and iodine are extensively used, in alkaline medium,[15,39,74-78] acidic medium,[34,39,79,80] or in neutral medium or organic solvent.[8,9,39,45,81-92] Other reagents commonly used include mercuric salts,[65,71,93-111] noble metal halides,[112,113] ferric salts,[8,9,81,114-117] potassium permanganate[8,12,14,18,56,65,79,84,91,102,105,118-136] and chromic anhydride.[18,137] Nitric acid, nitrous acid, nitrates, and nitrous fumes represent another large group of oxidants used.[8,12,14,18,43,75,89,92,119,127,138-147] Miscellaneous other reagents are also used,[6,10,72,83,134,139,148-155] and in other cases thione sulfur is replaced by oxygen in organic reagents via cyclic intermediates.[156-158]

IV. PRODUCTS OF REACTION

In some cases, especially by treatment with hydrogen peroxide, or peracetic acid under acidic conditions, the exocyclic thione group is replaced by hydrogen. The sulfur atom is eliminated as an oxidized species, usually sulfate. The organic moiety is left as a stabilized, usually aromatic, cation. This method has been widely used for thiopyran-2-thiones (Table VIII), 1,2-dithiole-3-thiones (Table X), 1,3-dithiole-2-thiones (Table XI) and isothiazoline-3-and-5-thiones (Table XVI). *e.g.*



(57)

The added hydrogen atom is derived from the acetic acid used as a solvent; or from the peracetic acid.[64] Thus reaction in monodeuteroacetic acid ($CH_3 \cdot CO_2D$) of 1,2-dithiole-3-thiones gave 3-deutero-1,2-dithiolium salts. In some heterocyclic mercaptans, particularly of nitrogen heterocycles, the mercapto group is lost, and the corresponding heterocycle is obtained which is unsubstituted in the position originally occupied by the mercapto group. In some non-aromatic examples, particularly 1,3-dithiolane-2-thiones, the thione function is reduced to a methylene group, although other sites are oxidized.[155]

No exhaustive evidence is available on intermediates in these reactions, but sulfines (thione-S-oxides, see below) have been determined in many cases, and are almost certainly the intermediates in others. Noble metal halides ($AuCl_3$, H_2PtCl_6), and nitric acid may also produce such reduced compounds, but no information is available on intermediates.

In another class of products obtained, an oxygen atom simply replaces the thione or thiol sulfur atom. Thus, a thione may give the corresponding "oxo" compound, beit a thiolactone, lactone, lactam or ketone, and mercaptans give the corresponding hydroxy compounds. Sulfines or related structures are almost certainly intermediates in these reactions. Recent evidence[159] also indicates that sulfenes (thione-S,S-dioxides) are the next oxidative stage at least in a few examples. Whether the reaction product obtained on treatment of thione with peracetic acid is the reduced product above, or "oxo" product has been correlated with the absence or presence resp. of other fused aromatic rings and electron withdrawing groups or substituents.[160] It appears that in a limited number of cases the presence of σ trivalent nitrogen favors reduced product.

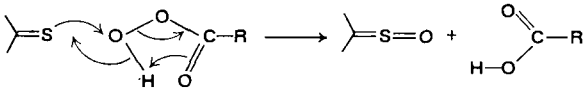
"Oxo" products are obtained by treatment with a variety of other reagents, particularly mercuric salts. These probably function by reaction with the heterocyclic thione to produce mercuri-thio derivatives of heterocyclic cations, or uncharged heterocyclic molecules, comparable to products found in the reaction of heterocyclic mercaptans with mercuric nitrate.[161] These mercurithio compounds then undergo nucleophilic attack by oxygen containing species to form "oxo" products by elimination of mercury containing substituents. Such mercury derivatives are often used in the purification of heterocyclic thiones.

Protonation by mineral acids, followed by nucleophilic attack probably accounts for the conversion by sulfuric acid[162] and the reaction with chlorine or bromine is probably similar, with initial formation of 1:1, thione: halogen adducts[69,70,85] which undergo nucleophilic attack with displacement of halide. Use of a variety of chlorine containing organic reagents also leads to formation of "oxo" compounds. Initial salt formation by these seems reasonable.

Permanganate treatment of thiones also leads to "oxo" compound formation. Presumably the reaction is comparable to that with olefines, with initial formation of a cyclic manganate ester. Reaction of permanganate with compounds which can tautomerize to thiols has been reported.[153,158] Initial attack by mercaptan on ethylene oxide is suggested, to give a substituent with a β-hydroxyethylthio substituent. A simple exchange mechanism has been proposed.[158] However, the reaction of an isothiazoline-3-thione with benzonitrile oxide leading to isothiazoline-3-one proceeds *via* a dipolar mechanism.[156] A spiran intermediate which decomposes to form isothiazoline and phenylisothiocyanate is suggested.

Disulfide product formation is common when compounds may exist as thiol forms and is comparable to the oxidation of simple thiols. Reagents used include iodine, or halogen in the presence of alkali, although dilute hydrogen peroxide and iodine have also been used. Suitable thiols are formed by thione-thiol tautomerism, or in some cases by processes akin to hemi-ketal formation, involving attack of an alcohol on a thione to generate a thiol. The oxidation is also effected by ferric chloride, ferricyanide or aerial oxidation.

Sulfines (thione–S–oxides) are the products obtained in a number of examples, and are almost certainly intermediates in further oxidation. It is also suggested that these are intermediates in the conversion of acyclic thiones to "oxo" compounds,[164] and this may hold for certain heterocyclic thiones. Hydrogen peroxide and per-acids are almost invariably used as oxidizing agents. An intramolecular proton transfer mechanism, such as has been suggested for sulfide to sulfoxide oxidations, seems reasonable.[165]

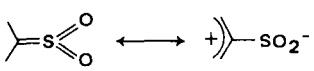


In a few cases lead tetraacetate has been used. Various oxidation mechanisms have been proposed to account for sulfines and other products of the reaction,[155] among then "oxo" compounds. These writers do not take into account possible direct sulfine-to-"oxo" compound conversion as has been suggested above and suggest that the different products of the reactions depend on different degrees of polarization of the thione group.

Like acyclic sulfines,[164,166] cyclic sulfines should be capable of geometrical isomerism, but no isolation of isomers appears to have been reported. In many cases these could exist mainly as sulfenic acid or sulfenate forms by tautomerism or resonance, and these forms due to ready rotation would be incapable of such isomerism. Indeed for the isomerization of acyclic sulfines a rotational mechanism is favored over inversion.[167] The bulk of evidence for acyclic sulfines appears to favor the sulfine over sulfenate form,[168] but aromatic stabilization would favor the sulfenate form in many cyclic cases.

Further oxidation of sulfine should produce sulfenes. These have not been isolated, but their transitory existence in a variety of aliphatic reactions

has been established,[169] and recent evidence[159] indicates their probable intermediacy in the oxidation of benzopyran-2-thiones by hydrogen peroxide or per-acids. It is also conceivable that in some cases there should be appreciable stabilization by resonance with forms having charge separation (sulfinates) especially where the aromatic ring acquires aromatic character.



Such forms are akin to sulfonates (see below).

The most highly oxidized products obtained have three oxygen atoms attached to the sulfur atom. Such compounds, which have been termed "thiotrioxides", have been isolated from the oxidation of many nitrogen-containing heterocycles and are sulfonic acids or sulfonates of heterocyclic cations. It is possible that these may be precursors of products where hydrogen or oxygen replaces the original thione sulfur atom. The first of these could arise by processes related to aromatic desulfonation, and the latter by nucleophilic attack of an oxygen containing species. Some "thiotrioxides" are known to be converted by treatment with sulfides to thiones.[170–172] Reagents used to prepare these "thiotrioxides" include hydrogen peroxide or potassium permanganate. In one interesting series of compounds, the pyridine-4-thiones, the presence of halogen in a system which when unsubstituted is oxidized to sulfonate, leads to formation of 4-pyridone.[50a,b] This may be explained by enhanced nucleophilic attack and displacement of sulfate or sulfite.

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