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MILD AND SELECTIVE OXIDATIONS WITH POLYSTYRENE-BOUND DIARYL SELENOXIDE

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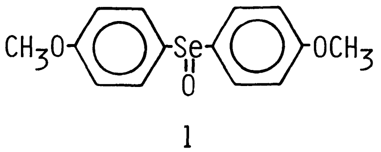
Polystyrene-bound diaryl selenoxide is shown to behave as a mild oxidizing agent for thiol to disulfide, sulfide to sulfoxide, phosphine to phosphine oxide, and hydroquinone to benzoquinone. In addition, it effects solvent-dependent reactions of thioamide to nitrile in usual solvent and to thiadiazole in acetic acid.

Selenoxides have recently been recognized to be mild oxidizing agents, though they and their reduced species are very often toxic and intractable.[1,2] The use of such reagents immobilized on polymer-resins would provide significant advantages, including decreased volatility, simplification of product work-up, and recovery and recycle of the spent reagent. Michels et al. reported the use of polymer-supported selenoxide, as only one example, for oxidation of 2-methylnaphthalene to 2-naphthaldehyde.[3] In connection with the versatile oxidizing abilities of bis(*p*-methoxyphenyl)selenoxide **1**,[1] we have studied on the reactivity of polymer-bound diaryl selenoxide **2**.



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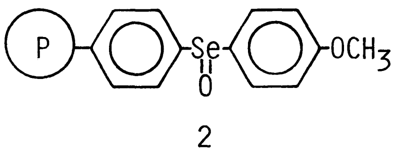

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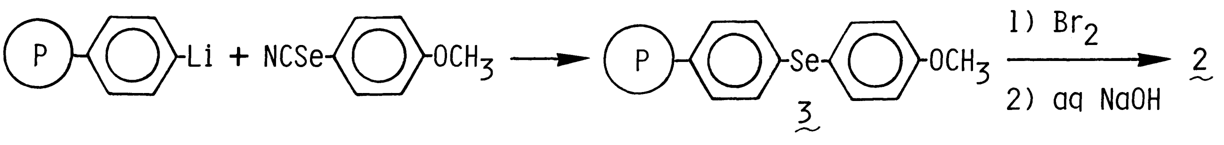
Polystyrene-bound diaryl selenoxide **2** was prepared by treatment of 1% cross-linked polystyryllithium resin[4] with *p*-methoxyphenylselenocyanate,[5] followed by bromination and hydrolysis of the resulting polystyrene-bound selenide **3**.[6]



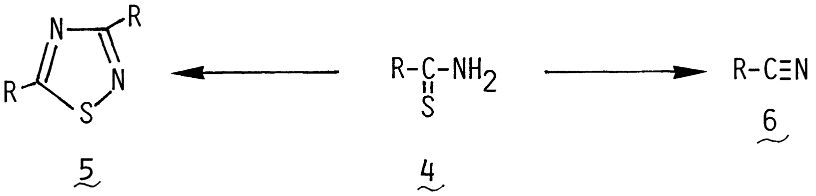
The polymeric reagent **2** like monomeric counterpart **1**[1] readily oxidized thiol to disulfide, sulfide to sulfoxide, phosphine to phosphine oxide, and hydroquinone to benzoquinone under very mild conditions. These results are summarized in Table 1. The reduced reagent could be recovered as selenide **3** by filtration and reused after oxidation with no apparent loss.

Table 1. Oxidations of thiol, sulfide, phosphine, and hydroquinone with polystyrene-bound selenoxide 2 at room temperature

Run	Substrate	Solvent	Time/h	Product	Yield/%[a,b]
1	C_6H_5SH	CH_2Cl_2	1.5	$(C_6H_5S)_2$	95 (90)
2	$C_6H_5CH_2SH$	CH_2Cl_2	1.5	$(C_6H_5CH_2S)_2$	93 (94)
3	$n\text{-}C_{16}H_{33}SH$	CH_2Cl_2	3	$(n\text{-}C_{16}H_{33}S)_2$	97 (95)
4	$NH_2CH_2CH_2SH$	CH_2Cl_2	1.5	$(NH_2CH_2CH_2S)_2$	100 (89)
5	$HOCH_2CH_2SH$	CH_2Cl_2	1.5	$(HOCH_2CH_2S)_2$	97 (92)
6	$(C_6H_5CH_2)_2S$	CH_3COOH	3.5	$(C_6H_5CH_2)_2SO$	98 (89)
7	$(C_6H_5)_3P$	CH_2Cl_2	3.5	$(C_6H_5)_3PO$	87 (99)
8	*p*-Hydroquinone	CH_3COOH	12	*p*-Benzoquinone	63 (87)
9	3,5-Di-*t*-butyl catechol	CH_3COOH	4.5	3,5-Di-*t*-butyl *o*-benzoquinone	96 (99)

a) Isolated yield.
b) For comparison, the yields of oxidations with selenoxide 1 are given in parentheses (Ref. 1).

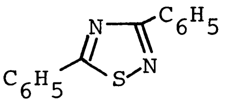
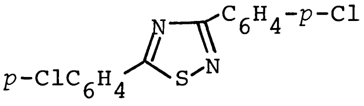
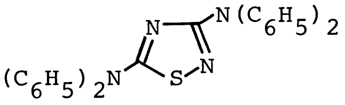
We earlier found a unique reaction of thioamide 4 to thiadiazole 5 with selenoxide 1 in ethanol or acetic acid at room temperature.1) However, such reaction with polymeric reagent 2 occurred only in acetic acid at higher temperature (75 °C). Some results are shown in Table 2. On the other hand, a similar treatment in usual solvents such as ethanol, methanol, acetonitrile, benzene, and ethyl acetate surprisingly yielded nitrile 6 as main product.



A wide variety of thioamides involving thioureas underwent the dehydrosulfurization to nitriles as shown in Table 3 (Runs 1-10).7) Sym-diphenylthiourea (Run 11) and tetramethylthiourea (Run 12), structurally incapable of forming nitriles, were smoothly oxidized to the corresponding ureas.

The present results reveal a marked dependency of reaction type on the choice of solvent used to swell the polymer. Two reaction mechanisms A and B are conceivable for formation of thiadiazole 5 and nitrile 6, respectively. The definitive difference arises from whether the initial adduct 7 of thioamide and selenoxide can react with another thioamide, then leading to thiadiazole 5, or degrade spontaneously to nitrile 6. It is obvious on the basis of the reaction with monoselenoxide 1 that Mechanism A is energetically favorable over Mechanism B. In the case of the reaction with polymeric reagent 2, the steric hindrance of polymer lattice probably prevents access of the reaction

Table 2. Oxidations of thioamides to thiadiazoles with polystyrene-bound selenoxide 2 in acetic acid at 75°C

Run	Substrate	Time/h	Product	Yield/%[a]
1	$C_6H_5CSNH_2$	24		84
2	p-$ClC_6H_4CSNH_2$	6		80
3	$(C_6H_5)_2NCSNH_2$	24		73

a) Isolated yield.

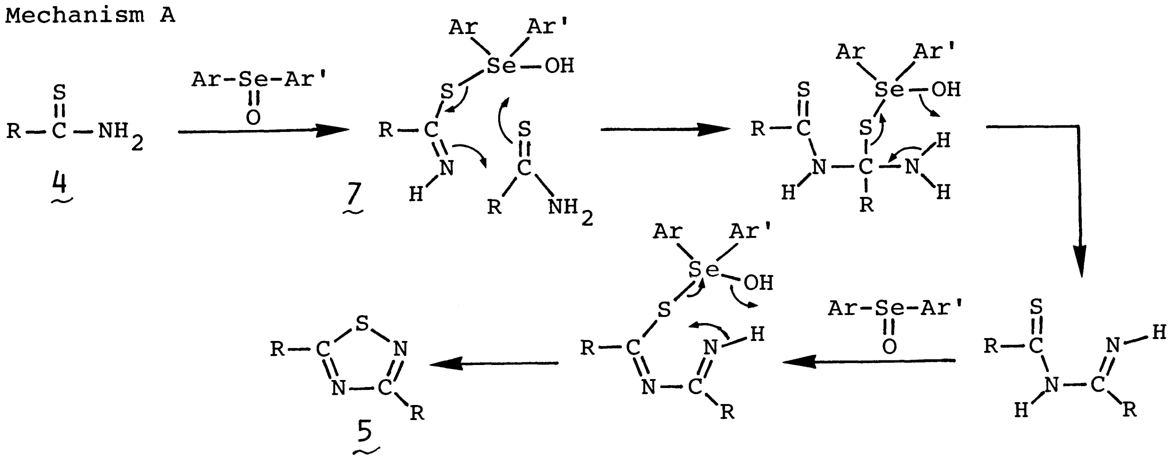
Table 3. Oxidations of thioamides to nitriles with polystyrene-bound selenoxide 2

Run	Substrate	Solvent	Temp/°C	Time/h	Product	Yield/%[a]
1	$C_6H_5CSNH_2$	EtOH	reflux	20	C_6H_5CN	84
		CH_3CN	75	12		37
		Benzene	75	12		82
		$CH_3COOC_2H_5$	75	12		50
2	p-$NO_2C_6H_4CSNH_2$	EtOH	reflux	24	p-$NO_2C_6H_4CN$	98
3	p-$ClC_6H_4CSNH_2$	EtOH	reflux	24	p-ClC_6H_4CN	88
4	o-$ClC_6H_4CSNH_2$	EtOH	reflux	24	o-ClC_6H_4CN	95
5	p-$CH_3OC_6H_4CSNH_2$	EtOH	reflux	24	p-$CH_3OC_6H_4CN$	96
6	n-$C_{17}H_{35}CSNH_2$	EtOH	reflux	24	n-$C_{17}H_{35}CN$	94
7	$C_6H_5CH_2CSNH_2$	EtOH	reflux	24	$C_6H_5CH_2CN$	69
8	Thionicotinamide	EtOH	reflux	24	3-Cyanopyridine	88
9	$C_6H_5NHCSNH_2$	MeOH	reflux	24	C_6H_5NHCN	85[b]
10	$(C_6H_5)_2NCSNH_2$	MeOH	reflux	8	$(C_6H_5)_2NCN$	88
11	$C_6H_5NHCSNHC_6H_5$	MeOH-CH_2Cl_2	RT	12	$C_6H_5NHCONHC_6H_5$	82
12	$(CH_3)_2NCSN(CH_3)_2$	CH_3COOH	RT	12	$(CH_3)_2NCON(CH_3)_2$	66

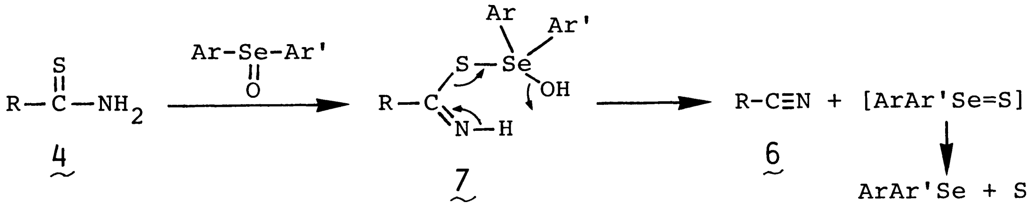
a) Isolated yield.
b) Yield contained that (42%) of triphenylisomelamine which was formed by trimerization of phenylcyanamide; A. W. Hofmann, Ber., 18, 3217 (1885).

site of adduct 7 to another thioamide in usual solvents. On the other hand, the acidity of acetic acid seems to promote the access reaction, as opposed to the steric effect. This is supported by an additional experimental result that treatment of thiobenzamide with polymeric reagent 2 in ethanol containing a small amount of hydrochloric acid gave 3,5-diphenyl-1,2,4-thiadiazole in 78% yield.

Mechanism A



Mechanism B



References

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2) A. G. Abatjoglou and D. R. Bryant, Tetrahedron Lett., 22, 2051 (1981); F. Ogura, T. Otsubo, K. Ariyoshi, and H. Yamaguchi, Chem. Lett., 1983, 1833; K. Takaki, M. Yasumura, and K. Negoro, J. Org. Chem., 48, 54 (1983); K. Ariyoshi, Y. Aso, T. Otsubo, and F. Ogura, Chem. Lett., 1984, 891; L. Syper and J. Młochowski, Synthesis, 1984, 747.

3) R. Michels, M. Kato, and W. Heitz, Makromol. Chem., 177, 2311 (1976).

4) M. J. Farrall and J. M. J. Fréchet, J. Org. Chem., 41, 3877 (1976).

5) O. Behaghel and M. Rollmann, J. Prakt. Chem., 123, 336 (1929).

6) Elemental analysis for selenium revealed that the polymer 2 contained 1.5 mequiv. of Se per gram.

7) Although earlier methods for dehydrosulfurization of thioamide to nitrile are often applicable to conversion of amide into nitrile, the present reaction is specific for thioamide; M. Lim, W. Ren, and R. S. Klein, J. Org. Chem., 47, 4594 (1982) and references cited therein.

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