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Polymer-Supported Diaryl Selenoxide and Telluroxide as Mild and Selective Oxidizing Agents

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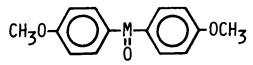
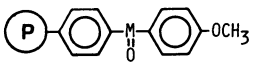
Polystyrene-bound diaryl selenoxide and telluroxide have been prepared, which behaved as mild oxidizing agents for thiols to disulfides, phosphines to phosphine oxides, hydroquinone and catechol to *p*- and *o*-benzoquinones, and thioketones to oxo compounds. The telluroxide completed these reactions in shorter periods or under milder conditions than the selenoxide. In addition, they effected novel solvent-dependent reactions of thioamides involving thioureas to 1,2,4-thiadiazoles or to nitriles. In nonacidic solvents, the dehydrosulfurization to nitriles occurred in preference to the oxidative dimerization to 1,2,4-thiadiazoles, but an acidic solvent such as acetic acid promoted the latter reaction.

Although organoseleniums[1] and telluriums[2] have recently received much attention as new synthetic reagents, most of their low-molecular species are extremely stinking and toxic. The immobilization of such reagents on polymer-resins would not only avoid the difficulties arising from volatility, but also provide some additional advantages including simplification of product work-up and recycle of the used reagents. There have been nevertheless known few examples of polymer-supported seleniums[3,4] and none of polymer-supported telluriums. Selenoxides[5-7] and telluroxides[8] have been recently recognized to have effective oxidizing abilities due to their weak chalcogen–oxygen bonds relative to sulfoxides. In particular, we and Barton et al. reported bis(*p*-methoxyphenyl) selenoxide **1a**[7] and telluroxide **1b**,[8] respectively, as new and versatile



1a M=Se
1b M=Te



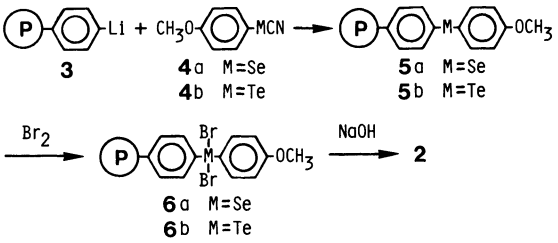
2a M=Se
2b M=Te

oxidizing agents. From the viewpoint of the practical use, we have designed the immobilization of these reagents on polymer-resins. Michels et al. already reported polymer-supported diphenyl selenoxide, but its reactivity has been revealed only for oxidation of 2-methylnaphthalene to 2-naphthaldehyde.[3] Here we report on the facile syntheses of polystyrene-bound diaryl selenoxide **2a** and telluroxide **2b** and on their reactivities toward various compounds as compared to monomeric counterparts **1a** and **1b**.[9]

Results and Discussion

Polystyrene-bound diaryl selenoxide **2a** and telluroxide **2b** were conveniently prepared as shown in Scheme 1. Poly(*p*-lithiostyrene) **3** was readily accessible from partial bromination of 1% cross-linked polystyrene resin, followed by halogen-metal exchange with butyllithium according to the method reported by Farrall and Fréchet.[10] Treatment of **3** with *p*-methoxyphenyl selenocyanate **4a**[11] gave a polymeric selenide **5a**, which was then converted via selenium dibromide **6a** into a light brown polymer of selenoxide **2a**. The infrared spectrum of **2a** closely resembled that of **5a**, but indicated a strong Se=O absorption at 820 cm^{-1}.[3] A polymeric telluroxide **2b** was similarly synthesized, starting from reaction of poly(*p*-lithiostyrene) **3** and *p*-methoxyphenyl tellurocyanate **4b**.[12] In contrast to well-defined Se=O absorptions, Te=O absorptions were obscure in the infrared spectrum of **2b**.

Both of the polymeric reagents **2a** and **2b**, like monomeric counterparts **1a** and **1b**, were inert to simple amines, amides, alcohols, and phenols, but readily oxidized thiols to disulfides, phosphine to phosphine oxides, and hydroquinone and catechol to *p*- and *o*-benzoquinones in dichloromethane, chloroform, or acetic acid as a swelling solvent at room temperature. In addition, **2a** converted sulfides into sulfoxides in acetic acid, while **2b** did not behave similarly.[13] These results are summarized in Table 1. The spent reagents could be recovered as the reduced species **5a** or **5b** by simple filtration and reused after



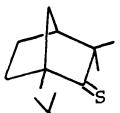
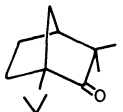
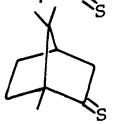
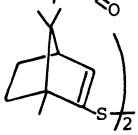
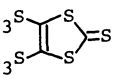
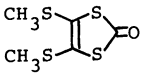
3 **4a** M=Se **4b** M=Te **5a** M=Se **5b** M=Te **6a** M=Se **6b** M=Te **2**

Scheme 1.

Table 1. Oxidations of Thiols, Phosphines, Hydroquinones, and Sulfides with Polymer-Supported Selenoxide **2a** or Telluroxide **2b** at RT

Run	Substrate	Reagent	Solvent	Time/h	Product	Yield/%
1	C_6H_5SH	**2a**	CH_2Cl_2	1.5	$(C_6H_5S)_2$	95
		2b	CH_2Cl_2	0.6		95
2	p-$NH_2C_6H_4SH$	**2b**	CH_2Cl_2	3	(p-$NH_2C_6H_4S)_2$	89
3	$C_6H_5CH_2SH$	**2a**	CH_2Cl_2	1.5	$(C_6H_5CH_2S)_2$	93
		2b	CH_2Cl_2	0.5		92
4	n-$C_{16}H_{33}SH$	**2a**	CH_2Cl_2	3	(n-$C_{16}H_{33}S)_2$	97
5	$NH_2CH_2CH_2SH$	**2a**	CH_2Cl_2	1.5	$(NH_2CH_2CH_2S)_2$	100
		2b	CH_2Cl_2	0.6		98
6	$HOCH_2CH_2SH$	**2a**	CH_2Cl_2	1.5	$(HOCH_2CH_2S)_2$	97
		2b	CH_2Cl_2	0.6		98
7	$(C_6H_5)_3P$	**2a**	CH_2Cl_2	3.5	$(C_6H_5)_3PO$	87
		2b	AcOH	2		99
8	(n-$C_4H_9)_3P$	**2b**	$CHCl_3$	0.6	(n-$C_4H_9)_3PO$	89
9	Hydroquinone	**2a**	AcOH	12	p-Benzoquinone	63
10	3,5-Di-t-butylcatechol	**2a**	AcOH	4.5	3,5-Di-t-butyl-o-benzoquinone	96
		2b	$CHCl_3$	0.8		96
11	$(C_6H_5CH_2)_2S$	**2a**	AcOH	3.5	$(C_6H_5CH_2)_2SO$	98
12	(n-$C_4H_9)_2S$	**2a**	AcOH	3	(n-$C_4H_9)_2SO$	87

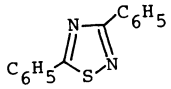
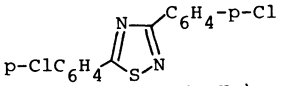
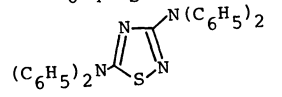
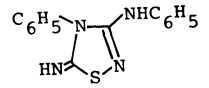
Table 2. Oxidations of Thiones and Thioesters with Polymer-Supported Selenoxide **2a** or Telluroxide **2b**

Run	Substrate	Reagent	Solvent	Temp	Time/h	Product	Yield/%
1	$C_6H_5CC_6H_5$ (S)	**2a**	$CHCl_3$	Reflux	6	$C_6H_5CC_6H_5$ (O)	30
		2b	$CHCl_3$	RT	1		98
2		**2a**	$CHCl_3$	Reflux	20		30
		2b	$CHCl_3$	RT	3		93
3		**2a**	$CHCl_3$	RT	20		66
		2b	CH_2Cl_2	RT	3.5		44
4		**2a**	CH_2Cl_2	Reflux	8		71
		2b	CH_2Cl_2	Reflux	6		84
5		**2a**	$ClCH_2CH_2Cl$	Reflux	36		trace
		2b	$ClCH_2CH_2Cl$	Reflux	36		71
6	$C_6H_5COCH_3$ (S)	**2a**	$CHCl_3$	Reflux	12	$C_6H_5COCH_3$ (O)	0
		2b	CH_2Cl_2	RT	5		91

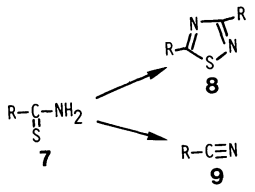
oxidation. The appreciable decrease of their activities was not observed even over ten recycles. Table 1 indicates that telluroxide **2b** completed reactions in shorter periods than selenoxide **2a**, reflecting the weaker Te=O bond relative to Se=O bond. The difference in reactivity between the two reagents became marked in the reactions toward thioketones. As shown in Table 2, telluroxide **2b** could smoothly convert thioketones and thioesters into the corresponding oxo compounds. As an exceptional case, thiocamphor was preferentially converted into a divinyl disulfide, being induced via enethiolization (Run 3). On the other hand, the selenoxide **2a** was less reactive toward most of the thioketones and failed to react with 4,5-bis(methylthio)-1,3-dithiole-2-thione (Run 5) and methyl thiobenzoate (Run 6) even under forced conditions.

It has become apparent that monomeric selenoxide

Table 3. Oxidations of Thioamides to Thiadiazoles with Polymer-Supported Selenoxide **2a** or Telluroxide **2b** in Acetic Acid

Run	Substrate	Reagent	Temp/°C	Time/h	Product	Yield/%
1	$C_6H_5CSNH_2$	**2a**	75	24		84
		2b	RT	12		53
2	p-$ClC_6H_4CSNH_2$	**2a**	75	6		80
		2b	RT	5		31[a]
3	$(C_6H_5)_2NCSNH_2$	**2a**	75	24		73
		2b	RT	5		0[b]
4	$C_6H_5NHCSNH_2$	**2b**	RT	12		97

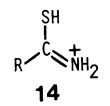
a) p-Chlorobenzonitrile was obtained in 47% yield as an acompanying product. b) Reaction at 75 °C resulted in dehydrosulfurization to give $(C_6H_5)_2NCN$ in 93% yield.



Scheme 2.

1a and telluroxide **1b** undergo different types of reactions toward thioamides involving thioureas as shown in Scheme 2. For example, reaction of thiobenzamide **7** (R=Ph) with **1a** in ethanol at room temperature gave 3,5-diphenyl-1,2,4-thiadiazole **8** (R=Ph) in 86% yield.[7] On the other hand, a similar treatment with **1b** gave benzonitrile **9** (R=Ph) in 78% yield. Polymeric selenoxide **2a**, unlike monomeric counterpart **1a**, hardly effected such oxidative dimerization, and permitted the formation of thiadiazole **8** in acetic acid at 75 °C. Some results are shown in Table 3. Treatments in usual solvents such as ethanol, acetonitrile, benzene, ethyl acetate, and 1,2-dichloroethane favored dehydrosulfurization to nitriles **9**. The best yield (84%) of benzonitrile from thiobenzamide was realized in refluxing ethanol. A wide variety of primary thioamides and thioureas were thus convertible into the corresponding nitriles in high yields as shown in Table 4. *N,N'*-Diphenylthiourea (Run 11) and tetramethylthiourea (Run 12), structurally incapable of forming nitriles, were smoothly oxidized to the corresponding ureas. The polymeric telluroxide **2b**, as a whole, behaved like the polymeric selenoxide **2a**, though the reaction conditions were much milder. Tables 3 and 4 also demonstrate the results of the oxidative dimerization and dehydrosulfurization, respectively, at room temperature. Table 3 shows that the oxidative dimerization with **2b** is not so effective and specific as that with **2a**. For example, treatment of p-chlorothiobenzamide with **2b** in acetic acid (Run 2) gave 3,5-bis(p-chlorophenyl)-1,2,4-thiadiazole (31%), together with p-chlorobenzonitrile (47%). Furthermore, *N,N*-diphenylthiourea did not undergo any oxidative dimerization on treatment with **2b** in acetic acid and rather favored dehydrosulfurization at an elevated temperature (Run 3).

Two mechanisms A and B, which can explain the formation of thiadiazole **8** and nitrile **9**, respectively, are proposed in Scheme 3.[14] Both mechanisms are initiated by addition of the reagent **2** to thioamide **7**, leading to an adduct **10**. A definite difference arises from whether the adduct **10** can react with another thioamide **7** to give a termolecular intermediate **11**, leading via a few steps to thiadiazole **8**, or degrade spontaneously to nitrile **9**. Monomeric selenoxide **1a** favors pathway A, while monomeric telluroxide **1b** favors pathway B. The difference is presumably related to their oxidizing abilities. On the other hand, both polymeric reagents **2a** and **2b** take pathway B in usual solvents, regardless of their oxidizing abilities and degree of swelling. The steric hindrance of the polymer lattice presumably prevents access of the reaction site of adduct **10** to another thioamide **7**, resulting in spontaneous degradation to nitrile **9**. The different reaction type in acetic acid is attributable to its acidity. The protonation of thioamide **7** to iminium **14** is expected to facilitate



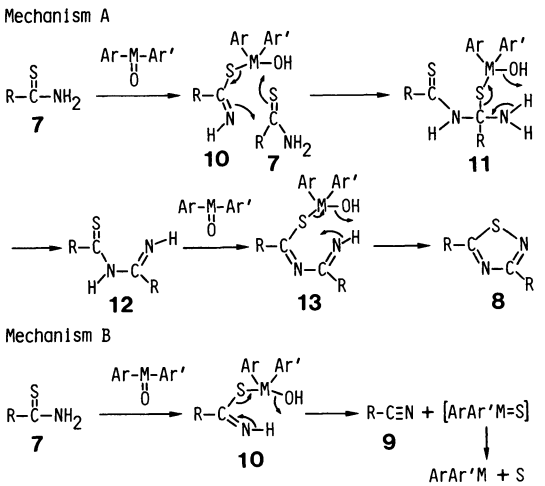
14

pathway A, because **14** is much more susceptible to nucleophilic attack of adduct **10** than **7**. This was supported by an additional experimental result that the dehydrosulfurization of thiobenzamide **7** (R=Ph) with polymeric selenoxide **2a** to benzonitrile **9** (R=Ph) in ethanol was depressed by addition of a

Table 4. Oxidations of Thioamides to Nitriles with Polymer-Supported Selenoxide **2a** or Telluroxide **2b**

Run	Substrate	Reagent	Solvent	Temp/°C	Time/h	Product	Yield/%
1	$C_6H_5CSNH_2$	**2a**	EtOH	Reflux	20	C_6H_5CN	84
		2a	MeCN	75	12		37
		2a	Benzene	75	12		82
		2a	AcOEt	75	12		50
		2a	$ClCH_2CH_2Cl$	75	12		33
		2b	CH_2Cl_2	RT	1		90
		2b	$CHCl_3$	RT	1		62
		2b	MeOH	Reflux	1		72
2	*p*-$CH_3OC_6H_4CSNH_2$	**2a**	EtOH	Reflux	24	*p*-$CH_3OC_6H_4CN$	96
		2b	CH_2Cl_2	RT	1		93
3	*p*-$ClC_6H_4CSNH_2$	**2a**	EtOH	Reflux	24	*p*-ClC_6H_4CN	88
		2b	CH_2Cl_2	RT	1		97
4	*o*-$ClC_6H_4CSNH_2$	**2a**	EtOH	Reflux	24	*o*-ClC_6H_4CN	95
		2b	CH_2Cl_2	RT	1		98
5	*p*-$NO_2C_6H_4CSNH_2$	**2a**	EtOH	Reflux	24	*p*-$NO_2C_6H_4CN$	98
		2b	CH_2Cl_2	RT	1		96
6	$C_6H_5CH_2CSNH_2$	**2a**	EtOH	Reflux	24	$C_6H_5CH_2CN$	69
		2b	CH_2Cl_2	RT	1		98
7	*n*-$C_{17}H_{35}CSNH_2$	**2a**	EtOH	Reflux	24	*n*-$C_{17}H_{35}CN$	94
		2b	CH_2Cl_2	RT	1		92
8	Thionicotinamide	**2a**	EtOH	Reflux	24	3-Cyanopyridine	88
9	$C_6H_5NHCSNH_2$	**2a**	MeOH	Reflux	24	C_6H_5NHCN	85[a]
10	$(C_6H_5)_2NCSNH_2$	**2a**	MeOH	Reflux	8	$(C_6H_5)_2NCN$	88
		2b	CH_2Cl_2	RT	24		95
11	$C_6H_5NHCSNHC_6H_5$	**2a**	MeOH-CH_2Cl_2	RT	12	$C_6H_5NHCONHC_6H_5$	82
		2b	CH_2Cl_2	RT	3.5		94
12	$(CH_3)_2NCSN(CH_3)_2$	**2a**	AcOH	RT	12	$(CH_3)_2NCON(CH_3)_2$	66

a) Yield contained that (42%) of 2,4,6-triimino-1,3,5-triphenyl-hexahydro-1,3,5-triazine which was formed by ready trimerization of phenylcyanamide; Ref. 22.



Scheme 3.

small amount of hydrochloric acid, forming instead 3,5-diphenyl-1,2,4-thiadiazole **8** (R=Ph) in 78% yield. In contrast, some of oxidative dimerizations with polymeric telluroxide **2b** in acetic acid competed with dehydrosulfurizations because of its relatively stronger oxidizing ability, indicating that the selectivity of either pathway A or B depends on a subtle balance of steric and electronic effects.

It has been thus understood that polymer-supported diaryl selenoxide **2a** and telluroxide **2b** like monomeric counterparts **1a** and **1b** behave as mild and selective oxidizing agents and complement each other owing to their different reactivities. In addition, they have turned out to effect novel solvent-dependent reactions of thioamides involving thioureas to 1,2,4-thiadiazoles or to nitriles. Although several methods for the oxidative dimerization of thioamides to 1,2,4-thiadiazoles[15] and for the dehydrosulfurization of thioamides to nitriles,[16] have so far been developed, they require relatively severe reaction conditions or highly reactive reagents which may affect other functional groups. The present methods using polymer-supported reagents **2a** and **2b** conveniently complement the preceding procedures, because of their wide applicability, high selectivity, and operational simplicity.

Experimental

Material. Polystyrene resin used in this research was 1% divinylbenzene-styrene copolymer, Bio-Beads S-Xl, purchased from Bio-Rad Laboratories. It was converted into poly(*p*-lithiostyrene) **3** according to the procedure of Farrall and Fréchet.[10] Most of the substrates examined in the oxidations with polymeric reagents **2a** and **2b** were commercially available. Thiobenzophenone, thiofenchone, thiocamphor, and methyl thiobenzoate (Runs 1—3,6 of Table 2) were obtained from reactions of the corresponding ketones[17] and ester[18] with Lawesson's reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide. 4,5-Bis(methylthio)-1,3-dithiole-2-thione (Run 5 of Table 2) was accessible from reaction of carbon disulfide with sodium, followed by methyl iodide.[19] Substituted thiobenzamides, phenylethanethioamide, and octadecanethioamide (Runs 2—7 of Table 4) were obtained from reactions of the corresponding amides with phosphorus pentasulfide in dioxane.[16]

Preparation of Polymeric Selenide 5a. Poly(*p*-lithiostyrene) resin **3**, in situ prepared from 5.0 g of partially brominated polystyrene containing 3.0 mequiv of bromine per gram,[10] was swollen in 50 ml of dry THF in a nitrogen atmosphere. After a solution of *p*-methoxyphenyl selenocyanate **4a**[11] (5.1 g, 24 mmol) in 10 ml of dry THF was added, the slurry was stirred at room temperature for 30 min and then at 60 °C overnight. The resin was collected by filtration, and washed successively with THF, 1:1 THF–water, water, again THF, and finally MeOH. After dryness under reduced pressure at 60 °C, a light brown resin of selenide **5a** (5.69 g) was obtained. Elemental analysis for selenium revealed that the resin contained 1.5 mequiv of Se per gram.

Preparation of Polymeric Selenoxide 2a. A solution of bromine (1.92 g, 12 mmol) in 10 ml of CCl_4 was dropwise added into a suspension of the resin **5a** (5.0 g) swollen in 30 ml of CCl_4. The slurry was stirred at room temperature for 4.5 h. The resulting selenium dibromide **6a** was collected by filtration, and washed successively with CCl_4 and THF. It was then mixed with 50 ml of THF and 10 ml of 15% NaOH aq, and refluxed overnight. The resin was collected by filtration, and washed once with THF, repeatedly with 1:10 THF–water until the washings turned neutral, and finally with MeOH. After dryness under reduced pressure at 60 °C, a light brown resin of selenoxide **2a** (4.9 g) was obtained. IR (KBr disk); 820 cm^{-1} (Se=O).

Preparation of Polymeric Telluride 5b. In a similar manner as described for polymeric selenide **5b**, a reddish yellow resin of telluride **5b** (8.05 g) was obtained from reaction of poly(*p*-lithiostyrene) **3**, in situ generated from 8.0 g brominated polystyrene (3.0 mequiv of bromine per gram), and *p*-methoxyphenyl tellurocyanate **4b**[12] (8.0 g, 31 mmol). Elemental analysis for C (75.50%) and H (6.11%) indicated that the resin contained the degree of 1.3 mequiv functionalization per gram.

Preparation of Polymeric Telluroxide 2b. In the quite same way as described for the preparation of polymeric selenoxide **2a**, a brown resin of telluroxide **2b** (8.1 g) was obtained via tellurium dibromide **6b** from telluride **5b** (8.0 g).

General Procedure for Oxidations with Polymeric Selenoxide 2a or Telluroxide 2b. An oxidizable substrate (0.5 mmol) was mixed with 20% excess of polymeric reagent **2a** or **2b** swollen in 10 ml of a solvent specified for each reaction. The mixture was treated under such conditions as described in Tables 1, 2, 3, or 4. After the reaction was completed, the spent reagent was removed by suction filtration, and washed throughly with the same solvent as used in the reaction. The filtrate and washings were combined and concentrated in vacuo. The residue was subjected to short column chromatography on silica gel or gel permeation liquid chromatography to give the corresponding pure product. All the products were characterized by comparison of their melting points and spectral data with those of the authentic samples, which were commercially available except divinyl disulfide (Run 3 of Table 2),[8] 1,3-dithiolan-2-one (Run 4 of Table 2),[20] 4,5-bis(methylthio)-1,3-dithiol-2-one (Run 5 of Table 2),[21] 3,5-diphenyl-1,2,4-thiadiazole (Run 1 of Table 3),[7] 3,5-bis(*p*-chlorophenyl)-1,2,4-thiadiazole (Run 2 of Table 3),[21] 3,5-bis(diphenylamino)-1,2,4-thiadiazole (Run 3 of Table 3),[7] 5-imino-4-phenyl-3-phenylamino-4,5-dihydro-1,2,4-thiadiazole (Run 4 of Table 3),[7] phenylcyanamide (Run 9 of Table 4),[22] and diphenylcyanamide (Run 10 of Table 4).[23]

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