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Bis(*p*-methoxyphenyl) Selenoxide as a Mild and Selective Oxidizing Agent

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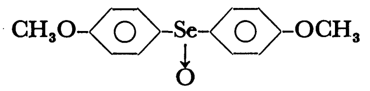
Synopsis. The title compound oxidized thiols to disulfides, sulfides to sulfoxides, hydroquinone or catechol to benzoquinones, and phosphine to phosphine oxide in high yields under very mild conditions. In addition, it functioned as a useful reagent for the syntheses of 1,2,4-thiadiazole derivatives from thioureas or thioamides.

Although the chemistry of organoseleniums is growing rapidly,[1)] little attention has been paid to the use of selenoxides as an oxidizing agent for organic syntheses. Selenoxides are usually unfavorable because of their nasty smell, but more reactive due to the greater basicity of the seleninyl oxygen than sulfoxides. For example, dimethyl selenoxide, dibenzyl selenoxide, or diphenyl selenoxide oxidized amines,[2)] anilines,[3)] catechols,[4)] sulfides,[5)] phosphines,[6)] and thiones[6,7)] unlike the sulfur counterparts.



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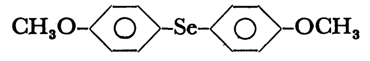

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Bis(*p*-methoxyphenyl) selenoxide **1** is an odorless, tractable material, and accordingly expected to be of practical use as an oxidizing agent. We now report the reactivity of **1** as shown in Table 1. Like the preceding selenoxides, **1** oxidized sulfides to sulfoxides, hydroquinone or catechol to benzoquinones, and phosphine to phosphine oxide in high yields. In addition, **1** effected the oxidation of thiols to disulfides under very mild conditions, in contrast to the fact that sulfoxides did it under forced conditions.[8)] The main by-product was bis(*p*-methoxyphenyl) selenide **2**, which could be used to regenerate **1**. On the other hand, **1** did not react with amines, anilines, phenylhydrazines, alcohols, and simple phenol.

The milder oxidizing properties of **1** relative to the preceding selenoxides were demonstrated by the reactions with thiones. For example, dimethyl selenoxide and dibenzyl selenoxide oxidized thiouracil **3** to uracil **4**[6)] and thiourea to urea,[7)] respectively. On the other hand, **1** effected milder oxidation to convert thiouracil **3** to 2,2′-dithio-di-4(3*H*)-pyrimidone **5**, and thiourea **6** to 3,5-diamino-1,2,4-thiadiazole **7**. As shown in Table

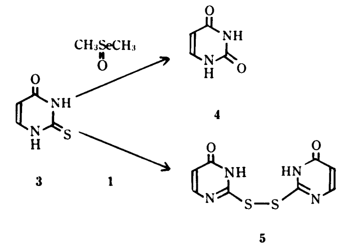
TABLE 1. OXIDATION OF THIOLS, SULFIDES, PHOSPHINE, HYDROQUINONE, CATECHOL, AND THIOURACIL BY **1** AT ROOM TEMPERATURE

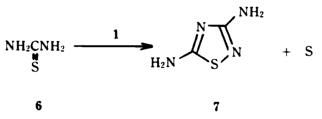
Material	Product	Time / min	Solvent	Yield / %	MP θ_m/°C
PhSH	PhSSPh	10	CH_2Cl_2	90	60
$PhCH_2SH$	$(PhCH_2S)_2$	30	CH_2Cl_2	94	69—70
n-$C_{16}H_{33}SH$	$(n$-$C_{16}H_{33}S)_2$	30	CH_2Cl_2	95	54—55
$NH_2CH_2CH_2SH$	$(NH_2CH_2CH_2S)_2$	30	CH_2Cl_2	89	Oil
$HOCH_2CH_2SH$	$(HOCH_2CH_2S)_2$	10	CH_2Cl_2	92	24—24.5
$(PhCH_2)_2S$	$(PhCH_2)_2SO$	40	AcOH	89	130—131
$(n$-$C_{12}H_{25})_2S$	$(n$-$C_{12}H_{25})_2SO$	60	AcOH	87	88—88.5
Ph_3P	Ph_3PO	15	CH_2Cl_2	99	154—155
Hydroquinone	*p*-Benzoquinone	40	MeOH	87	112—113
3,5-Dibutylcatechol	3,5-Dibutyl-*o*-benzoquinone	120	EtOH–Ether (1 : 1)	97	111—112
3	**5**	100	EtOH–$CHCl_3$ (1 : 1)	74	190(dec)

TABLE 2. OXIDATION OF THIOUREAS AND THIOAMIDES BY **1**[a)]

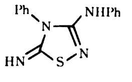
Material	Product	Solvent	Yield / %	Mp(lit) θ_m/°C
$H_2NC(S)NH_2$	**7**	EtOH	78	168—170 (169—171)[c)]
$PhNHC(S)NH_2$	**8**	AcOH	60	179—180 (181)[d)]
PhNHC(S)NHPh	**9**	EtOH	84	51—52 (51—52)[e)]
$Ph_2NC(S)NH_2$	**10**	EtOH	88	154—155.5 (155)[f)]
$CH_3C(S)NH_2$	**11**	EtOH	45[b)]	Oil
$PhC(S)NH_2$	**12**	EtOH	86	89.5—90 (90)[g)]

a) Reaction time 1 h at room temperature. b) Gas chromatographic analysis. c) F. Kurzer, *J. Chem. Soc.*, **1955**, 1. d) D. S. Hector, *Ber.*, **22**, 1176 (1889). e) Ref. 11. f) T. Charkrabarti and S. Chandra De, *J. Indian Chem. Soc.*, **5**, 661 (1928). g) A. W. Hofmann, *Ber.*, **2**, 645 (1869).





2, some thiadiazole derivatives were prepared not only from thioureas but from thioamides. Phenylthiourea reacted with **1** in a somewhat different way to give 5-imino-4-phenyl-3-phenylamino-4,5-dihydro-1,2,4-thiadiazole **8** as the exclusive product. *N,N'*-Diphenylthiourea can not lead to thiadiazole structure, but was smoothly oxidized by **1** to afford 2,4-diphenyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine **9**. Hector reported in 1890 that **9** was synthesized by treatment of the same thiourea with hydrogen peroxide,⁹⁾ but later the product was claimed to be a different compound **13**.¹⁰⁾ Very recently Kinoshita *et al.* succeeded the formation of **9** by use of benzoyl peroxide as an oxidizing agent.¹¹⁾ The yield (84%) of **9** by the present method is much higher than that (13%) by Kinoshita's method.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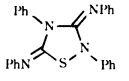
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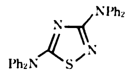
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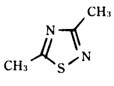
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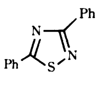
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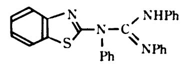
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Experimental

Melting points are uncorrected. Solvents are of reagent grade. All products were confirmed by comparison of the melting points and spectroscopic data with those of the authentic samples or the reported data.

Bis(*p*-methoxyphenyl) selenide **2** was readily prepared from a reaction mixture of anisole, selenium dioxide, and water according to the procedure of Boyd *et al.*,¹²⁾ and converted to bis(*p*-methoxyphenyl) selenoxide **1** by oxidation with sodium periodate.¹³⁾

*General Method of Oxidation by Bis(*p*-methoxyphenyl) Selenoxide 1.* A typical procedure is described in the reaction of thiobenzamide as below. A mixture of thiobenzamide (0.137 g, 1.0 mmol) and **1** (0.339 g, 1.1 mmol) in 6 ml of ethanol was stirred for one hour at room temperature. After the solvent was evaporated, the residue was taken up in chloroform and the insoluble sulfur was removed by filtration. The preparative gel-permeation liquid chromatography (JAI LC-08) of the filtrate using chloroform as eluent gave first bis(*p*-methoxyphenyl) selenide **2** in almost quantitative yield and then 3,5-diphenyl-1,2,4-thiadiazole **12** in 86% yield, colorless needles from methanol.

For isolation and purification in some of the other reactions, column chromatography was employed as well.

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