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Reduction of Selenoxides with Thione Reagents

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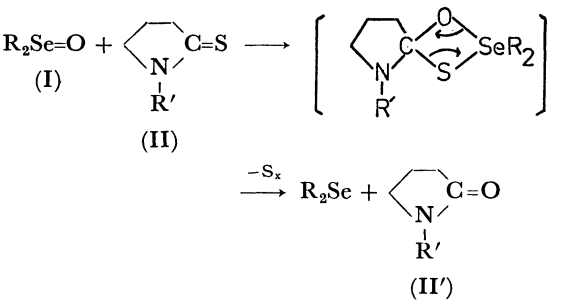
Synopsis. The reaction of selenoxides with various thione compounds such as carbon disulfide, thioamides and thioureas was found to give selenides. The reaction mechanism was discussed.

It is widely known that sulfoxides are deoxygenated by various powerful reducing reagents.[1] Carbon disulfide, a weak reducing reagent, can never deoxygenate dialkyl and diaryl sulfoxides. Selenoxides are more basic and reactive as compared with analogous sulfur compounds due to the more polar nature of the Se=O bonding than the S=O bonding. Thus, diphenyl selenoxide is more basic and readily reducible by phosphines than the most basic sulfoxide, DMSO.[2,3] However, few reports have been given so far on the chemical behavior of selenoxides toward weak reducing reagents. We report here the results of the reactions of diphenyl and dibenzyl selenoxides with various thione reagents.

Results and Discussion

Diphenyl and dibenzyl selenoxides (I) reacted at room temperature with equimolar amounts of thioamides such as 1-phenyl- and 1-methylpyrrolidine-2-thiones (II-Ph, -Me) and *N*,*N*-dimethylthioacetamide to give the selenides and the corresponding amides with extrusion of elemental sulfur (Table 1). The results indicate that, in marked contrast to sulfoxides, the oxides undergo a facile deoxygenation even with agents having weak reducing ability.



In a different way, selenoxides were readily reduced with carbon disulfide to give the corresponding selenides and chloroform-insoluble colorless precipitates without deposit of elemental sulfur. The results are summarized in Table 2. The reaction of dibenzyl selenoxide with small amounts of carbon disulfide or phosphorous pentasulfide in chloroform produced dibenzyl selenide

TABLE 1. REDUCTION OF DIPHENYL AND DIBENZYL SELENOXIDES (I) WITH THIONE REAGENTS (II and III) IN $CHCl_3$ AT ROOM TEMPERATURE

(I)	Thione reagent	Mole ratio[a]	Reaction time	Product (isolated%)
$Ph_2Se=O$	II-Ph	1	2 h	Ph_2Se(89), II'-Ph(83), S_x[b]
$Ph_2Se=O$	II-Me	1	2 h	Ph_2Se(73), II'-Me(73), S_x[b]
$Ph_2Se=O$	III	1	10 h	Ph_2Se(75), III'(0), III(78)
$Tol_2Se=O$	III	1	10 h	Tol_2Se(89), III'(12), III(48)
$(PhCH_2)_2Se=O$	II-Ph	1	5 min	$(PhCH_2)_2Se$(92), II'-Ph(82), II-Ph(3), S_x[b]
$(PhCH_2)_2Se=O$	II-Ph	0.1	5 min	$(PhCH_2)_2Se$(14), II'-Ph(75)[c]
$(PhCH_2)_2Se=O$	$MeC(S)NMe_2$	1	3 h	$(PhCH_2)_2Se$(93), MeC(O)NMe(93)
$(PhCH_2)_2Se=O$	III	1	4 h	$(PhCH_2)_2Se$(85), III'(21), III(63)
$(PhCH_2)_2Se=O$	$(Me_2N)_2CS$	1	2 h	$(PhCH_2)_2Se$(87), $(Me_2N)_2CO$(21), $(Me_2N)_2CS$(37)

a) [II or III]/[I]. b) Yields not determined. c) Based on the amount of the thione (II-Ph) used.

TABLE 2. REACTION OF DIPHENYL AND DIBENZYL SELENOXIDES (I) WITH CARBON DISULFIDE IN $CHCl_3$ AT ROOM TEMPERATURE

(I)	Mole ratio[a]	Reaction time	Product (isolated %)
$Ph_2Se=O$	10	10 h	Ph_2Se(47), oil(12),[c] Ph_2SeO(16)
$Ph_2Se=O$	b)	10 min	Ph_2Se(77), oil(21)[c]
$Tol_2Se=O$	b)	5 min	Tol_2Se(74), oil[c]
$(PhCH_2)_2Se=O$	3	12 h	$(PhCH_2)_2Se$(74), P(23)[d]
$(PhCH_2)_2Se=O$	0.1	24 h	$(PhCH_2)_2Se$(65), P(17)[d]
$(PhCH_2)_2Se=O$	1[e]	5 min	$(PhCH_2)_2Se$(96), P(0)[d]
$(PhCH_2)_2Se=O$	0.05[e]	3 h	$(PhCH_2)_2$(72), P(19)[d]

a) $[CS_2]/[I]$. b) CS_2 used as a solvent. c) Structure not identified. d) P denotes precipitate. e) The reaction with P_2S_5.

Table 3. The reaction of the precipitate (P) with thione reagents in $CHCl_3$ at room temperature

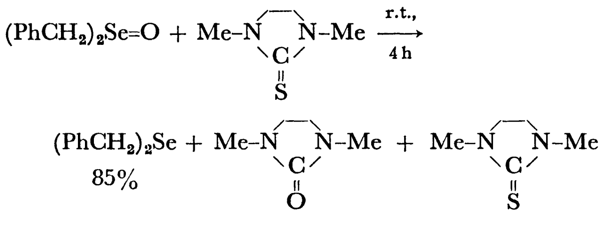
Thione	Mole ratio[a]	Reaction time	Products, isolated %		
			$(PhCH_2)_2Se$	II′ or III′	II or III
II-Ph	1	10 min	86	46	53
III	1	10 min	72	0	52[b]
$(Me_2N)_2C=S$	1	10 min	70	0	26[b]

a) [Thione]/[P]. b) Unidentified substances obtained.

and substantial amounts of precipitate, P (dec 115—117 °C). The elemental analysis of the precipitate gave no constant value, within analytical accuracy, with samples taken from different runs, but mostly agreed with a structure carrying five oxygen atoms per one dibenzyl selenide skeleton. This was further supported by the mass spectrum exhibiting the molecular peak at *m/e* 341 arising probably from $(PhCH_2)_2SeO_5$ (33% of base). The detailed structure is still not clear, but it involves $(PhCH_2)_2SeO_5$ as the most important species.

$$(PhCH_2)_2Se{=}O \xrightarrow[P_2S_5]{CS_2\ \text{or}} (PhCH_2)_2Se + \underset{(P)}{(PhCH_2)_2SeO_5}$$

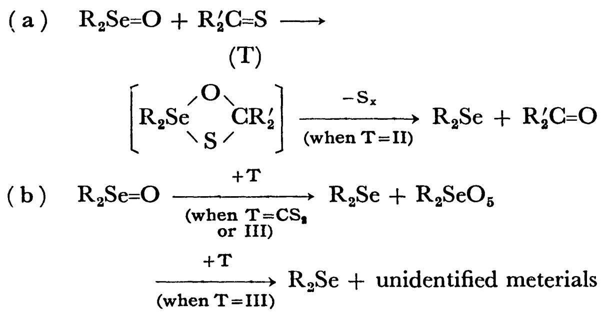
The results given in Table 1 indicate that the reaction of dibenzyl selenoxide with an equimolar amount of thiourea, 1,3-dimethylimidazolidine-2-thione (III), gave only about 20% yield of the corresponding urea derivative (III′) together with the selenide, accompanied by considerable recovery of the starting thione compound (III). The same is true for tetramethylthiourea. The fact that considerable amounts of the thione compounds were recovered unchanged implies that two reactions take place competitively: one producing dibenzyl selenide and the carbonyl compound, and the other catalytically affording the same selenide and, probably, the precipitate, which then reacts rapidly with the remaining thiourea to give the selenide. The fact, when the precipitate (P) itself was allowed to react with thioureas, dibenzyl selenide and a structure-unidentified product were obtained without being accompanied by the formation of the corresponding carbonyl compounds. The results are given in Table 3.



(III′) 21% (III) 63%

$$\underset{(P)}{(PhCH_2)_2SeO_5} + \text{III} \xrightarrow[10\,\text{min.}]{\text{r.t.,}} (PhCH_2)_2Se + \text{unidentified product}$$

It thus appears that, with thioamides having a labile thiocarbonyl group, Path a in Scheme 1 shown below is preferable for reduction and Path b, if operative, would be only minor, since the thioamides are almost completely consumed during the course of reaction. On the other hand, with carbon disulfide bearing stable C=S groups, the reaction proceeds mainly *via* Path b where no release of elemental sulfur is observed. The behavior of thioureas is intermediate between that of thioamides and carbon disulfide.



Scheme 1.

Experimental

Reaction of Diphenyl and Dibenzyl Selenoxides with Thione Compounds. A typical experimental procedure is as follows: 1-Phenylpyrrolidine-2-thione (177 mg, 1 mmol) was added at room temperature to a $CHCl_3$ (20 ml) solution of dibenzyl selenoxide (277 mg, 1 mmol). The reaction was followed by TLC. After the reaction was complete, evaporation of the solvent followed by preparative thin-layer chromatography of the residue gave dibenzyl selenide, 1-phenylpyrrolidone and the recovered thione in 92, 82 and 3% yields, respectively.

Some Physical Properties of the Precipitate (P). Mp: 115—117 °C; IR (KBr): 1100 (strong) cm^{-1}; NMR (d_6-DMSO): $\delta=7.27$ (s, 10H), 4.22 (q, 4H) ppm from external TMS; Elemental analysis: Found: (1) C, 49.16; H, 4.58. (2) C, 48.70; H, 4.66. (3) C, 49.83; H, 4.73%. Calcd for $C_{14}H_{14}O_5Se$: C, 49.27; H, 4.13. MS: 342 (M^+), 262. Calcd M: 342 assuming Se=80.

Reaction of Dibenzyl Selenoxide with Carbon Disulfide. Dibenzyl selenoxide was added at room temperature to 20 ml of a $CHCl_3$ solution containing CS_2 (238 mg, 3 mmol). After 12 h, a colorless precipitate was filtered off. The filtrate was concentrated. Preparative TLC of the residue gave dibenzyl selenide in 74% yield.

References

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