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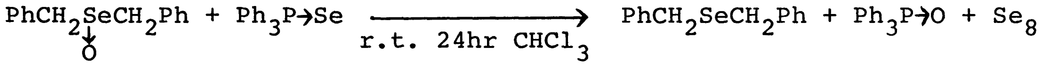
FACILE REDUCTION OF SELENOXIDE WITH PHOSPHINE SELENIDE

Keishi SAKAKI and Shigeru OAE
Department of Chemistry, University of Tsukuba, Ibaraki 300-31

Facile reduction of selenoxide with phosphine selenide gives corresponding selenide, phosphine oxide and elemental selenium and the reaction is presumed to proceed through substitution at the equatorial-equatorial position of phosphorus atom.

Various oxidations with dimethyl sulfoxide have been investigated for many years.1) Recently phosphine sulfide or selenide has been reported to be oxidized with dimetyl sulfoxide in the presence of acid or iodine to afford the corresponding phosphine oxide, dimethyl sulfide and elemental sulfur or selenium.2) Meanwhile, in the course of our continuous investigation on the reaction of the selenoxide,3) we have now examined a reaction of selenoxide with phosphine selenide. The reaction of selenoxide with phosphine selenide proceeded without any catalytic acid or iodine, and afforded the corresponding selenide and phosphine oxide with concomitant formation of elemental selenium. The overall reaction is illustrated by the following equation.



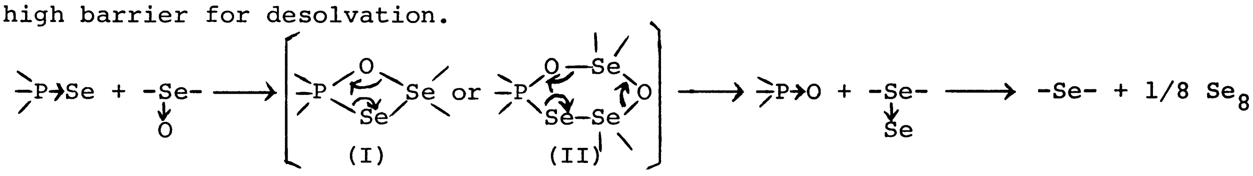
$$PhCH_2\underset{\downarrow O}{Se}CH_2Ph + Ph_3P{\rightarrow}Se \xrightarrow[\text{r.t. 24hr } CHCl_3]{} PhCH_2SeCH_2Ph + Ph_3P{\rightarrow}O + Se_8$$

An equimolar amount of triphenylphosphine selenide was added to the dibenzyl selenoxide in dry chloroform and the mixture was kept standing at room temperature. After the reaction was completed, the elemental selenium precipitated in the reaction was filtered off and the filtrate was treated on preparative thin layer chromatography (Kieselgel GF_{254}; $CHCl_3$ as eluent) to afford the corresponding selenide and phosphine oxide in nearly quantitatively. Results of the reaction under various conditions are listed in Table I.

Table I. The Products Analyses of the Reaction of Selenoxides with Phosphine Selenides under Various Conditions at Room Temperature.

	R_1-Se(O)-R_2		solv.	react. time (hr) 4)	products(%)		
					P→O	-Se-	Se_8
$Ph_3P{\rightarrow}Se$	$PhCH_2$	$PhCH_2$	$CHCl_3$	24	90	93	95
	Ph	$PhCH_2$	$CHCl_3$	24	92	93	98
	Ph	Ph	$CHCl_3$	13(day)	99	79	95
$Bu_3P{\rightarrow}Se$	$PhCH_2$	$PhCH_2$	$CHCl_3$	10(min)	93	87	91
			CH_2Cl_2	1	*5)	*5)	*5)
	Ph	Ph	$CHCl_3$	10(min)	84	97	91
			CH_2Cl_2	2.5	*5)	*5)	*5)
			CH_3COCH_3	12	*5)	*5)	*5)
Me n-Pr-P→Se Ph	Ph	Ph	$CHCl_3$	60	88	87	97

In order to obtain a rough picture of the reaction route, we compared the rate of the reaction in $CHCl_3$ with those in some other solvents. Inspection of Table I reveals that as the polarity of the solvent increased, the rate of the reaction decreased. This large solvent effect on the rate of the reaction may be attributable to desolvation, since the reactants contains polar P→Se and Se→O linkage and are highly solvated in polar media in ground state. Consequently when the reaction proceeds through a formation of non-polar intermediate (I) or (II) as shown below, the rate would be quite retarded in polar media due to the high barrier for desolvation.



Furthermore we have obtained an additional information relating to the intermediate (I) or (II) by the stereochemical investigation on phosphorus atom. When optically active methylphenyl-n-propylphosphine selenide ($[\alpha]_D^{25}=-13.0^\circ$, c=1.6, e.e.=65.9%6)) was treated with diphenyl selenoxide, the corresponding inverted phosphine oxide ($[\alpha]_D^{25}=+10.8^\circ$, c=2.1, e.e.=54.0%7)) was obtained: stereospecificity 81.9%. Because of the predominant inversion of configuration on phosphorus atom through the reaction we favoured the intermediate (II) in which the reaction proceeded through the equatorial-equatorial position on phosphorus atom.8)

Further detailed study for the reaction mechanism is being examined kinetically.

References and Notes

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4) Reactions were followed by the TLC spot for the phosphine selenide and the end points were determined by disappearance of the spot.
5) Reaction products were identified by comparison of the R_f values with those of the authentic samples on TLC plate.
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