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Reactions of Phosphonium Ylides with S_8 or Se in the Presence of Amines. Formation of Thioaldehydes or Selenoaldehydes

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The reaction of phosphonium ylides with elemental sulfur gave thioaldehydes which were successfully changed to corresponding thioamides when treated with secondary amines. On the other hand, the reaction of selenoaldehydes with secondary amines afforded bis(dialkylamino)methanes in good yields.

Phosphonium ylides (1) have been widely utilized for the synthesis of olefins¹⁾ and also known to react with sulfur to afford thiocarbonyl compounds.²⁾ The chemistry of thio-³⁾ (2) and selenoaldehydes⁴⁾ (3) has been of current interest. Recently, we have reported that the reaction of 1 with elemental selenium afforded symmetrical olefins via selenocarbonyl intermediates⁵⁾ and the reaction of 1 with episulfides also gave symmetrical olefins via thiocarbonyl intermediates.⁶⁾ Compounds 2 and 3 are very reactive and easily oligomerize to give trimers or complex mixture of polymers. The reactions of 2 and 3 with dienes produced the corresponding Diels-Alder adducts.^{3,4,6)} However, to our knowledge, relatively few reports concerning the reactivity of these compounds have appeared because of their instability. These results prompted us to investigate the reactivity of 2 and 3. In this communication, we would like to report that the reaction of 1 with S₈ or Se in the presence of amines afforded thioamides (4) and bis(dialkylamino)methanes (5) in good yields.

We first tried the reaction of 2 with amines: To a solution of carbomethoxymethylenetriphenylphosphorane (1a, 10 mmol) and morpholine (20 mmol) in toluene (25 ml) was added a solution of sulfur (10 mmol) in toluene (20 ml). After refluxing for 12 h, the reaction mixture was washed with water and evaporated to give the corresponding thioamide (4a) and triphenylphosphine sulfide in 75 and 90% yields, respectively. As shown in Table 1, compounds 4b-4e were prepared in a similar manner. Since 2 was known to be synthesized by the reaction of the corresponding sulfenyl chlorides with triethylamine, 3b we also carried out the same reaction starting from carbomethoxymethanethiol as a starting material. The same product 4a was obtained.



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Compound		Method ^{a)}		
Thioaldehyde	Amine		Thioamid	$e^{/}$ (yield/%)
R				
COOMe	Morpholine	А	<u>4</u> a	75
COOMe	Dimethylamine	A	4b	76
COOMe	Morpholine	В	4a	66
COOEt	Morpholine	A	4 <u>c</u>	73
p-NO2-C6H	morpholine	В	4d	90
Ph 2 0 4	Morpholine	A	4e	56 _b
Ph	Morpholine	В	4e	0.07

a) Method A; phosphonium ylide + sulfur: Method B; sulfenyl chloride + base b) Benzenesulfenylmorpholide was obtained in 68% yield.

Thioaldehydes were recently prepared by several groups: photolysis of phenacyl sulfide derivatives;^{3a)} reaction of sulfenyl chlorides with bases;^{3b)} reaction of Bunte salts with bases;^{3b)} thermolysis of thiolsulfinate.⁸⁾ However, there is no report on the synthesis of 2 from phosphonium ylides.⁹⁾ Milligan and Swan reported that the reaction of Bunte salts of carbamoyl derivatives with primary and secondary amines afforded thio-oxaamides and disulfides. They suggested that these compounds might be formed, in a complex manner, from thio-aldehydes intermediates.¹⁰⁾

We further tried the reaction of selenoaldehydes with secondary amines. Treatment of phosphonium ylides with elemental selenium resulted in the formation of selenoaldehydes, which further reacted with secondary amines to give bis(dialkylamino)methanes instead of selenoamides. (Table 2)



Table 2. Reaction of Selenoardenydes with Amines				
Ylide	Amine	Diamine ⁷⁾ (yield/%)		
COOMe COOEt Ph $p-NO_2-C_6H_4$	Morpholine Morpholine Morpholine Morpholine	5a 70 5b 76 5c 75 5d 68		

Table 2. Reaction of Selenoaldehydes with Amines

Several reports to generate selenoaldehydes have been made: variants of 1,2elimination reactions employing suitably substitutd precursors X-RCHSe-Y;⁴) reaction of sulfur ylides with elemental selenium;¹¹⁾ reaction of aromatic aldehydes with bis(trimethylsilyl)selenide.¹²⁾ However, there is no report on the reaction of <u>3</u> with amines.

As to the formation of $\frac{4}{2}$, the following mechanism is plausible: thioaldehydes were converted to the corresponding $\frac{5}{2}$ by treatment with amines in a similar manner to the reaction of amines with aldehydes.¹³⁾ The resulting $\frac{5}{2}$ further reacted with hydrogen sulfide produced to give $\frac{4}{2}$. In the case of selenoaldehydes, hydrogen selenide was too unstable to react with $\frac{5}{2}$. Mechanism:

$$\begin{array}{c} R \\ C=S + R'_2 NH \longrightarrow R \\ H \end{array} \begin{array}{c} R \\ C(NR'_2)_2 \end{array} \xrightarrow{H_2 S \text{ or } S} R-C-NR'_2 \end{array}$$

The above mechanism was confirmed by the following two reactions. When the reaction of 1a with S_8 in the presence of morpholine was carried out at 50 °C, 5a was isolated in 70% yield instead of 4a. Additionally, treatment of 5a with hydrogen sulfide afforded the corresponding thioamide 4a in 65% yield. The difference in the reactivity of selenoaldehyde and thioaldehyde might be owing to the reactivity toward 5: while the reaction of 5a with hydrogen sulfide or elemental sulfur gave thioamide (4a), the same reaction of 5a with selenium resulted in recovery of starting material quantitatively.

In summary, the reaction of thioaldehydes with amines gave the corresponding thioamides in good yields. On the other hand, the reaction of selenoaldehydes with secondary amines afforded bis(dialkylamino)methanes in good yields. References

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