

Reaction of *N,N*-Dialkylaminodimethylarsine and -stibine with β -Propiolactone—A Kinetic Study

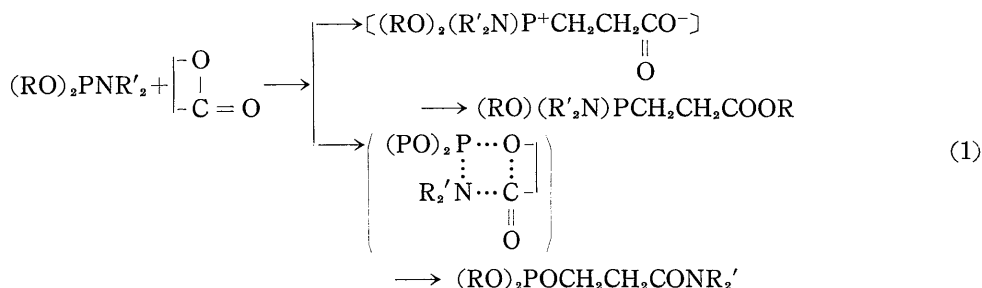
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The reaction of *N,N*-dialkylaminodimethylarsine and -stibine (metal amides: M-N) with β -propiolactone was studied by measuring the decrease of the amount of the β -propiolactone by IR spectrum. A 2nd order rate equation can be applied to this reaction. It was found that there was no linear relation between the rate constant and pKa value of the nitrogen atom of the metal amides. The reaction rate increased with increasing electron density on the nitrogen atom of the metal amides, and could be explained by Taft's equation; however, it seemed that the additional hyperconjugation effect played an important role in the reaction.

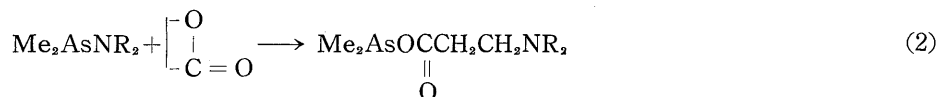
1. Introduction

During the course of studies of the reactions of group V organometal compounds, we found that aminophosphines showed an ambident nature in their reactions. On the other hand, β -propiolactone is well known to be cleaved at either the alkyl-oxygen bond or the acyl-oxygen bond and the mode of ring opening depends on the nature of the nucleophiles. McConnel and Coover reported that β -propiolactone reacted with trialkylphosphite to give 2-alkoxycarbonylethylphosphonate¹⁾ and it was also reported the reaction of dialkylphosphite with β -propiolactone took place through acyl-oxygen bond fission.²⁾ In these reactions, the phosphorus atom itself worked as a nucleophilic site. In regard to the reaction³⁾ of aminophosphine with β -propiolactone, we found previously that both the phosphorus atom and the nitrogen atom could be a nucleophilic site and the mode of the bond fission of β -propiolactone was explained by the soft and hard acid and base concept (SHAB).⁴⁾

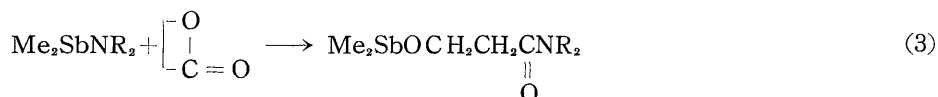


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The reactions of aminoarsine and aminostibine with β -propiolactone were also studied and the mode of ring opening of the β -propiolactone was found to be different in the two cases. In the case of the aminoarsine, β -propiolactone was cleaved at the alkyl-oxygen bond as shown in eq. (2),



but the aminostibine gave reaction products which were obtained through the acyl-bond fission of β -propiolactone (eq.(3)).



The kinetic studies of these reactions will give information regarding the properties of the group V elements. The reaction of *N,N*-dialkylaminodimethylphosphine with β -propiolactone gave only the polymer of β -propiolactone. Therefore, direct comparison of the three elements is impossible. In this work, the kinetic behavior of the reactions of *N,N*-dialkylaminodimethylarsine and -stibine with β -propiolactone were studied and the reaction mechanisms are discussed.

2. Experimental

Reagents *N,N*-dialkylaminodimethylarsine—Dimethylarsine chloride in ten times its volume of dry ether was added to an equivalent amount of lithium salt of secondary amine in ether, cooled in ice, and then the mixture was set aside at room temperature overnight. The lithium chloride was removed, the solvent was distilled off, and the product was distilled. The physical properties and the yield are tabulated in Table 1.

Table 1 The Physical Properties and Yield of Metal Amides

Compounds	°C/mmHg	Yield	n_D^{25}
$\text{Me}_2\text{AsNEt}_2$	81-82/100	52.0	1.4623
$\text{Me}_2\text{AsNBu}^n_2$	55-56/0.2	56.2	1.4679
$\text{Me}_2\text{AsNBz}_2$	118-119/0.1	77.4	1.5799
Me_2AsN (cyclo- C_6H_{11}) $_2$	90-91/0.2	49.0	1.4923
$\text{Me}_2\text{SbNMe}_2$	53-55/40	34.8	1.5157
$\text{Me}_2\text{SbNEt}_2$	67-68/25	28.0	1.4990
$\text{Me}_2\text{SbNPr}^n_2$	90-91/23	44.2	1.4983
$\text{Me}_2\text{SbNPr}^i_2$	72-73/18	67.5	1.4921
$\text{Me}_2\text{SbNBu}^n_2$	62-63/0.05	69.9	1.4951
$\text{Me}_2\text{SbNBu}^i_2$	44-45/0.18	53.2	1.4969
$\text{Me}_2\text{SbNBz}_2$	81-82/0.1	26.6	1.5036
Me_2SbN (cyclo- C_6H_{11}) $_2$	115-116/0.09	47.7	1.5889

N,N-Dialkylaminodimethylstibine, By the same method as in the case of aminoarsine, the aminostibines were obtained from dimethylstibine chloride and lithium salt of the secondary amine. The physical properties and the yield are also shown in Table 1. β -Propiolactone was obtained commercially and dried over calcium hydride and distilled before use.

Solvents were commercial materials and purified according to the standard methods.⁵⁾

A typical procedure of the Rate Measurements. A solution containing a known amount of *N,N*-dialkylaminodimethylarsine or -stibine in a given solvent and equivalent amount of β -propiolactone in two separate flasks were allowed to stand at given reaction temperature and then mixed quickly to start the reaction. Aliquot (each 0.5 ml) of this reaction mixture was pipetted out at relevant intervals of time and the amount of the residual β -propiolactone was determined by IR spectroscopy.

3. Results

The reaction of *N,N*-dialkylaminodimethylarsine with β -propiolactone gave dimethylarsenic 3-dialkylaminopropionate which showed a strong carbonyl absorption at 1700 cm^{-1} . Throughout the kinetic study in this experiment the carbonyl absorption always appeared at 1700 cm^{-1} in spite of the change of the alkyl group on the nitrogen atom and this showed that the mode of ring opening of the β -propiolactone was the same. The same phenomena were observed in the reactions of *N,N*-dialkylaminodimethylstibines with β -propiolactone where amide groups were formed showing an IR absorption at 1634 cm^{-1} .

Table 2 shows the effect of the change of the initial concentrations of *N,N*-dialkylaminodimethylstibine and of β -propiolactone on the rate constants.

Table 2 Effect of initial concentration of *N,N*-diethylaminodimethylstibine and β -propiolactone on the rate constant in chlorobenzene at 100°C

$[\text{Me}_2\text{SbNEt}_2]$ (mol/l)	$[\beta\text{-PL}]$ (mol/l)	k_2 (l/mol·hr)
0.05	0.05	9.43
0.025	0.05	10.57
0.05	0.025	9.94

These results suggest that the reaction obeys 2nd order kinetics (eq. (1)).

$$V = -\frac{d[\beta\text{-PL}]}{dt} = k_2[\text{M-N}][\beta\text{-PL}] \quad (4)$$

The 2nd order rate constants for several kinds of *N,N*-dialkylaminodimethylarsine and -stibine at various temperatures as well as activation parameters are summarized in Table 3 and Table 4, respectively, and in Fig. 1, the Arrhenius plots for some aminoarsines are shown.

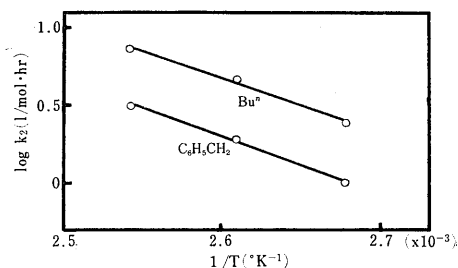
The rate constants of the reaction between *N,N*-dialkylaminodimethylarsine and -stibine and β -propiolactone in various solvents at 100°C are shown in Table 5 and the m values of the equation: $\log k_2 = m(1/\epsilon)$ are calculated to be -2.36 , and -3.36 for aminoarsine and aminostibine, respectively.

Table 3 Second order rate constants of the reactions between *N,N*-disubstituted aminodimethylstibine and β -propiolactone in chlorobenzene

[Me ₂ SbNR ₂] ₀ =[β -PL] ₀ =0.05 mol/l								
R	Me	Et	Pr ⁿ	Bu ⁿ	C ₆ H ₅ CH ₂	Bu ⁱ	Pr ⁱ	cyclo-C ₆ H ₁₁
pKa	10.64	10.98	11.00	11.25	—	10.63	10.64	—
σ^*	0.00	-0.100	-0.115	-0.130	+0.215	-0.125	-0.198	-0.15
Es	0.00	-0.07	-0.36	-0.38	-0.38	-0.93	-0.47	-0.79
k_2 (l/mol·hr)								
80° C	10.7	3.48	—	—	—	—	—	—
90° C	19.6	6.58	—	—	—	—	—	—
100° C	23.2	9.43	5.72	8.00	1.33	2.12	0.27	1.00
110° C	—	—	9.57	15.3	2.52	3.31	1.07	1.80
120° C	—	—	16.2	22.0	4.57	7.37	1.46	3.80
Ea (Kcal/mol)	10.2	13.1	15.2	14.8	18.0	18.1	24.8	19.5
log A	7.35	8.65	9.66	9.60	10.7	10.9	14.0	11.4

Table 4 Second order rate constants of the reactions between *N,N*-dialkylaminodimethylarsine and β -propiolactone in chlorobenzene

[Me ₂ AsNR ₂] ₀ =[β -PL] ₀ =0.05 mol/l				
R	Et	Bu ⁿ	C ₆ H ₅ CH ₂	cyclo-C ₆ H ₁₁
pKa	10.98	11.25	—	—
σ^*	-0.100	-0.130	+0.215	-0.15
Es	-0.07	-0.39	-0.38	-0.79
k_2 (l/mol·hr)				
100° C	4.01	2.43	1.00	0.38
110° C	—	4.74	1.97	—
120° C	—	7.28	3.27	—
Ea (Kcal/mol)	—	16.0	17.3	—
log A	—	9.80	10.2	—

**Fig. 1** Arrhenius plots for the reactions of *N,N*-dialkylaminodimethylarsine with β -propiolactone in chlorobenzene.**Table 5** Solvent effect on the reaction of *N,N*-diethylaminodimethylarsine with β -propiolactone at 100°C

	ϵ	k_2
<i>o</i> -dichlorobenzene	9.93	6.14
chlorobenzene	5.621	4.01
<i>n</i> -butyl ether	3.083	1.868

4. Discussion

In the reaction of M-N compounds (M: P, As, Sb and Bi), several reaction paths are possible because the elements M's and N belong to the group V elements and both have a lone pair of electrons and can act as nucleophilic sites, and also the elements M's can expand their octet and act as electrophilic site. As regards the reaction of M-N compounds with carbonyl compounds, several reaction paths will be considered, i.e., a: nucleophilic attack of the nitrogen atom on the carbon atom, b: nucleophilic attack of M on the carbon atom, c: electrophilic attack of M on the carbonyl or ester oxygen atom with the octet expansion of the M element. In fact, we have reported³⁾ that both the nitrogen atom and the phosphorus atom can act as a nucleophilic site in the reaction of dialkyldimethylphosphoramidate with β -propiolactone, as shown in eq. (1). A kinetic study⁶⁾ of the reaction of *N,N*-dialkylamino-diphenylphosphine with acetic anhydride suggested the four-centered reaction path where the nitrogen atom played an important role as a nucleophilic site and the phosphorus atom attacked the oxygen atom, expanding its octet. The reaction of aminoarsine and aminostibine with β -propiolactone can proceed through paths a or c, judging from the reaction products shown in eqs (2) and (3), so the reaction mechanism b can be discounted. If the reaction proceeds through the path c, the effect of the substituents on the nitrogen atom of M-N compound will differ greatly from the path a. When the nitrogen atom acts as a nucleophilic site, there are two kinds of electronic effects. If the transition state is much closer to the initial state, a linear relationship between the basicity of the amino group and the reaction rate will be expected. On the other hand, if the transition state is much closer to the product, Taft's equation will hold for these reactions. In the experiments reported

here, there is no close relationship between the reactivity and the basicity⁷⁾ of the amino groups. Taft's equations can hold for both reactions when the substituents are primary groups as

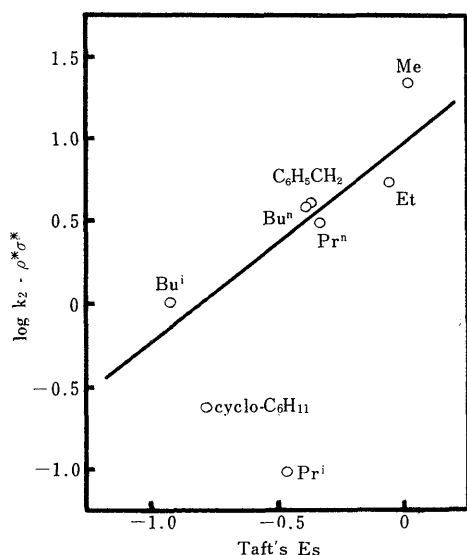


Fig. 2 The Taft relationship for the reactions of *N,N*-dialkylaminodimethylstibine with β -propiolactone.

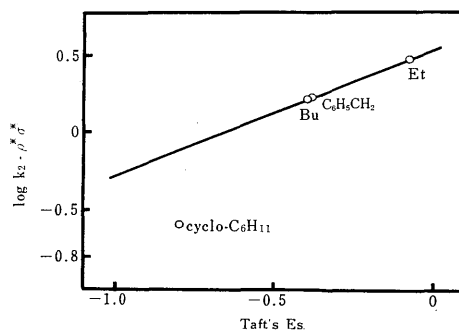
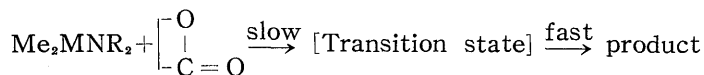


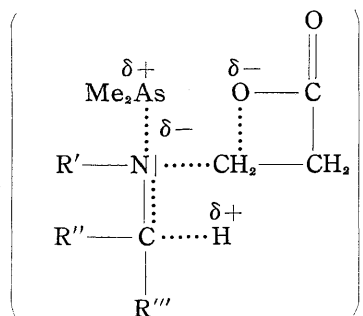
Fig. 3 The Taft relationship for the reactions of *N,N*-dialkylaminodimethylstibines with β -propiolactone

shown in Figs 2 and 3. The values of ρ^* are calculated to be -1.12 and -2.26 for the reactions of the aminoarsine and the aminostibine, respectively. Note that in the case that a methyl group is the substituent on a nitrogen atom, the reaction is more rapid than predicted by Taft's equation. On the other hand, the reactions are less rapid than predicted by Taft's equation, when substituents are secondary alkyl groups such as isopropyl and cyclohexyl groups. These phenomena can be explained by assuming that the electron density of the nitrogen atom is affected by the hyper-conjugation of the hydrogen atoms on the α -carbon atom. A methyl group has three hydrogen atoms and contributes to a great increase of the electron density on the nitrogen atom by the hyper-conjugation effect. Secondary alkyl groups have only one hydrogen atom, so the reactions are retarded greatly in the case that isopropyl or cyclohexyl groups are substituents. Similar phenomena were observed in the reactions of amines with methyl acetate⁸⁾ or ethylene carbonate,⁹⁾ and also in the reactions of *N,N*-dialkylaminodiphenylphosphine with acetic anhydride⁽³⁾ where the ρ^* value was found to be -0.194 . This $|\rho^*|$ value is rather small compared with the values for the aminolyses of methylacetate and ethylene carbonate (1.53 and 3.5 respectively). The steric requirement in the reaction of aminophosphine was much severer than in the case of the reaction of amines. The m value, i.e., susceptibility of the reaction rate to the solvent polarity, was found to be -1.3 . These phenomena supported the conclusion that in the reaction of a P-N compound with carbonyl compounds, the nitrogen atom played an important role as a nucleophile, but there was an interaction between the phosphorus atom of the aminophosphine and the carbonyl or ester oxygen, i.e. the reaction proceeded through a four-centered mechanism. The important roles of the nitrogen atom in the reactions of aminoarsine and aminostibine are well reflected in the large $|\rho^*|$ and $|m|$ values and in the fact that the main factor which controls these reactions is the electron density on the nitrogen atom. Therefore the path a is considered to be the main route for these reactions, and the following reaction scheme is supported by the above discussion.

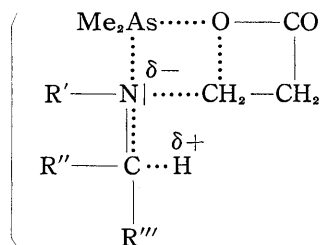


As regards the transition state, we can picture two possible structures [1] and [2], for aminoarsine, and [3] and [4], for aminostibine. In the case of the phosphorus amide, we have proposed the four-centered mechanism, but in the reaction of aminoarsine and aminostibine with β -propiolactone, the presence of ionic dipolar intermediates [1] and [3] can be reasonably inferred from the above discussions.

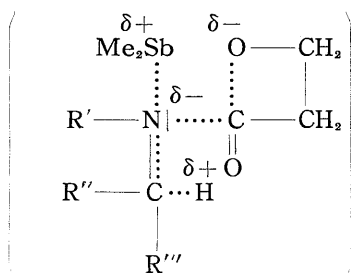
In order to explain the drastic change of fission mode of β -propiolactone, the principle of SHAB⁴⁾ attracts our attention, because β -propiolactone possesses both "hard" sp^2 carbonyl carbon atoms and "soft" sp^3 carbon atoms in the same molecule. Nucleophilic reagents such as nitrogen or oxygen are known to behave as "hard bases", when they react as free anions. The metal-nitrogen bonds of metalamides are



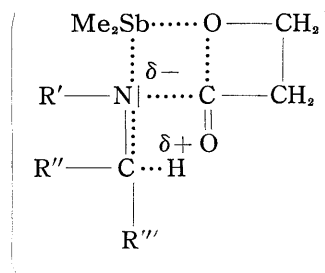
[1]



[2]



[3]



[4]

essentially covalent, so the degree of ionization is important in determining the hardness of the nitrogen atoms in metal amides. The degree of ionization is influenced by difference in electronegativity and in atomic size. Both effects give higher polar character to the Sb-N bond than to As-N bond. Therefore the nitrogen atom in aminostibines possesses a hard base character compared to that of aminoarsine, and cleaves the acyl-oxygen bond of β -propiolactone.

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