Kinetic Study of Addition Reactions of Trimethylsilyl- and Trimethylgermyl-amines with β-Propiolactone

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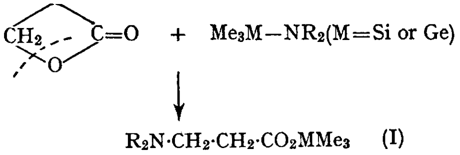
ADDITION reactions of β-propiolactone (β-PL) to trimethylsilyl- and trimethylgermyl-amines, giving trimethylsilyl(germyl) esters of *NN*-dialkyl-β-alanine (I) through the alkyl–oxygen bond cleavage of β-PL, have previously been reported.[1,2]

These addition reactions are slow enough to be followed kinetically, by determining the decreasing amounts of β-PL measured with the characteristic absorption of β-PL at 1833 cm.$^{-1}$.



Second-order kinetics obtain for the reaction of 0·1M mixtures of β-PL and *N*-trimethylsilyl-diethylamine, -piperidine, and -pyrrolidine, respectively, in ethylene dichloride. Results obtained are summarized in Table 1. It should be noted that the rate was enhanced with increasing basicity of silylamines which was assessed from the pK_a value of the parent secondary amine (diethylamine 10·98, piperidine 11·22, and pyrrolidine 11·27).

From the observation by Swain and Scott,[3] who obtained linear correlation between nucleophilic constant (n) of the several nucleophiles and log k_2, trimethylsilylamine is deduced to be a nucleophilic reagent on β-PL.

The effect of solvent was investigated for the reaction of β-PL with trimethylsilylpiperidine at 70°, and the results are shown in Table 2.

Since the increase of the solvent polarity accelerates the reaction, the transition state has dipolar character.

TABLE 1

Addition reaction of trimethylsilyl- and trimethylgermyl-amines $Me_3M–NR_2$, *with β-propiolactone in ethylene dichloride*

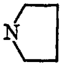
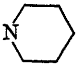
$Me_3M–NR_2$ M	NR_2	Temp. (°c)	10^3k_2 (l./mole.sec.)	E_a (kcal./mole)	ΔS^* (e.u./mole)
		65·0	0·610		
Si	NEt_2	70·0	0·913	20	−11
		72·0	1·09		
		75·0	1·48		
		65·0	3·47		
Si		67·0	3·87	13	−31
		70·0	4·63		
		72·0	5·28		
		62·0	3·85		
Si		65·0	5·43	22	−2
		70·0	8·53		
		73·0	11·0		
		55·0	3·14		
Ge	NEt_2	60·0	3·81	11	−41
		65·0	4·94		
		55·0	19		
Ge		60·0	23	11	−35
		65·0	30		

TABLE 2

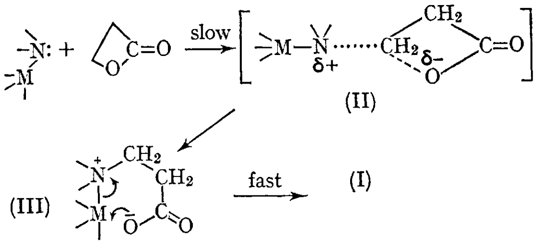
Solvent effect on the reaction of β-propiolactone with trimethylsilylpiperidine

Solvent	10^3k_2(l./mole.sec.)	$10^3(\epsilon - 1/2\epsilon + 1)$ (25°)
Toluene	0·457	2·40
Fluorobenzene	1·57	3·18
o-Dichlorobenzene	2·18	4·28
Ethylene dichloride	4·63	4·75

The kinetic study was extended to the reaction of germanium analogues and the results obtained are also included in Table 1. Two interesting points emerge, namely, the rate constants obtained for germanium analogues are eight to nine times higher than for the corresponding silicon analogues, and a similarity of the rate constant ratio for $[k(Me_3MNC_5H_{10})/k(Me_3MNEt_2)]$ at 65° is observed, *i.e.*, 5·7 for M = Si and 6·0 for M = Ge. The higher reactivity of Ge–N compounds compared with that of Si–N compounds cannot be ascribed to the small difference of electronegativity. It is reasonable to suppose that the nucleophilicity of Si–N compounds is lower than that of Ge–N compounds, on account of the larger contribution of $d\pi$–$p\pi$ conjugation in Si–N bond.

$$[\geq M–N\langle \longleftrightarrow \geq M^-=N^+\langle]$$

From the above results, together with the fact that the alkyl–oxygen bond fission of β-PL occurred with Si–N and Ge–N compounds, we suggest the following mechanism.



Nucleophilic attack of the nitrogen atom of trimethylsilyl(germyl)amines on the β-carbon of β-PL may play an important role in this reaction through dipolar transition state (II), giving betain-type intermediate (III) which is compatible with the fact that betain was obtained by the reaction of β-PL with tertiary amines.[4]

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[2] K. Itoh, S. Sakai, and Y. Ishii, *Tetrahedron Letters*, 1966, 4941.

[3] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, 1953, 75, 141.

[4] T. L. Gresham, J. E. Jansen, F. M. Shaver, R. A. Bankert, and F. T. Fiedorek, *J. Amer. Chem. Soc.*, 1951, 73, 3168.