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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS
VI. THE REACTION BETWEEN TRIMETHYLTIN METHOXIDE AND β-PROPIOLACTONE

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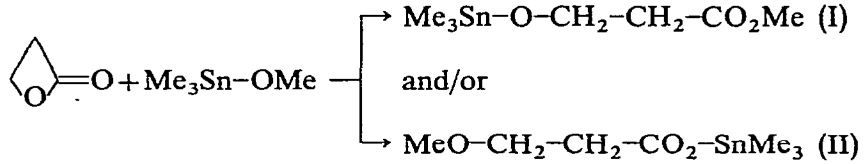
In the course of our studies on the addition reactions of Group IV organometallic compounds, it became clear that β-propiolactone was cleaved selectivily through alkyl–oxygen by (trimethylsilyl)-[1] or (trimethylgermyl)dialkylamine[2], but through acyl–oxygen fission by the trimethyltin analogue[2].

Several reactions involving addition of organotin alkoxides or oxides to various acceptor molecules containing polar double bonds such as isocyanates[3-5], carbonyl compounds[6,7], ketene[8], and diethoxyacetylene[9] have been described in the recent years. However, no report has been published on the reaction of trialkyltin alkoxide with β-propiolactone, and we have now studied the reaction of trimethyltin methoxide with β-propiolactone.

Two types of ring opening are possible for the reaction of β-propiolactone with trimethyltin methoxide, one giving methyl β-(trimethylstannoxy)propionate, (I), through acyl–oxygen bond cleavage, the other giving trimethyltin β-methoxypropionate, (II), through alkyl–oxygen cleavage:



$$+ Me_3Sn{-}OMe \rightarrow Me_3Sn{-}O{-}CH_2{-}CH_2{-}CO_2Me \text{ (I)} \text{ and/or } MeO{-}CH_2{-}CH_2{-}CO_2{-}SnMe_3 \text{ (II)} \quad (1)$$

It was found that the acyl–oxygen bond cleavage was preferred in β-propiolactone, and that the ratio was affected strikingly by the polarity of the medium.

The product ratio (I)/(II) in the reaction mixture could be determined from the relative intensity of the NMR signals due to the methoxycarbonyl proton in (I) and to the methoxy proton in (II). In order to know the accurate chemical shifts of the above two signals, the authentic samples of (I) and (II) were prepared by trimethylstannylation[10] of methyl β-hydroxypropionate, (IV), and β-methoxypropionic acid, (V), respectively. Both compounds (IV) and (V) were obtained from the methanolysis of β-propiolactone[11].

$$\underset{\text{(IV)}}{HO{-}CH_2{-}CH_2{-}COOMe} + Me_3Sn{-}NEt_2 \rightarrow \underset{\text{(I)}}{Me_3Sn{-}O{-}CH_2{-}CH_2{-}CO_2Me} + Et_2NH \quad (2)$$

$$\underset{\text{(V)}}{MeO{-}CH_2{-}CH_2{-}COOH} + Me_3Sn{-}NEt_2 \rightarrow \underset{\text{(II)}}{MeO{-}CH_2{-}CH_2{-}CO_2{-}SnMe_3} + Et_2NH \quad (3)$$

The chemical shifts of the methoxycarbonyl proton of (I) and the methoxy proton of (II) were τ 6.42 and 6.77 ppm, respectively.

Reaktions were carried out by mixing 2.00 millimoles of trimethyltin methoxide dissolved in 1.00 ml of solvent with 2.00 millimoles of β-propiolactone and heating at 70° for 4 hours. After the removal of solvent under reduced pressure, the residue was dissolved in carbon tetrachloride and the relative intensities of the singlets at τ 6.42 and 6.77 ppm were determined. Table 1 lists the ratios of two products (I)/(II) and the dielectric constants of the solvents[12].

It is seen that in any solvent, the quantity of (I), formed by the acyl–oxygen bond cleavage of β-propiolactone was larger than that of (II) formed by alkyl–oxygen bond fission. This conclusion was supported qualitatively from the infrared spectra of the reaction mixture, the carbonyl stretching frequency at 1740 cm^{-1} due to (I) being far more intense than that due to (II) at 1653 cm^{-1}.

TABLE 1

SOLVENT EFFECT ON THE MODE OF FISSION OF β-PROPIOLACTONE BY TRIMETHYLTIN METHOXIDE[a]

Solvent	*CO–O/CH_2–O (I/II)*	ε^b
Carbon tetrachloride	exclusively (I)	2.24
Benzene	365	2.28
Chloroform	33.0	4.80
Tetrahydrofuran	27.6	7.59[c]
Ethylene dichloride	18.3	10.3
Acetone[d]	8.93	20.7
Acetonitrile	3.97	37.5
γ-Butyrolactone	3.35	39.1

[a] $[\beta\text{-PL}]_0 = [Me_3SnOMe]_0 = 2.00$ millimoles, solvent 1.00 ml, 70° for 4 h. [b] See Ref. 12. [c] See Ref. 15. [d] Because of the low solubility of trimethyltin methoxide, this value was estimated by extrapolating from the values obtained with 1.5 and 3.0 ml of acetone.

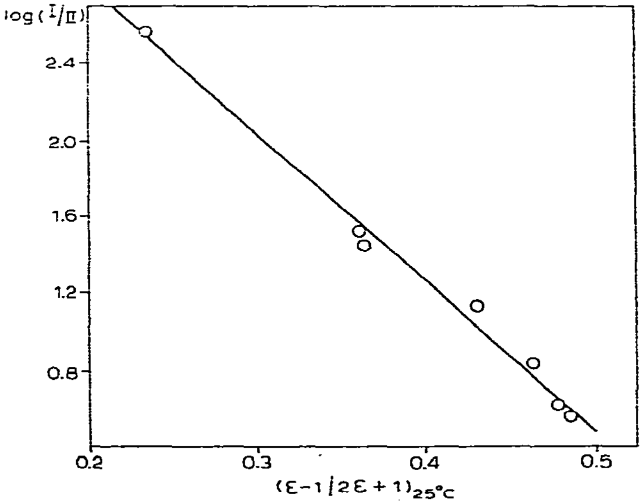


Fig. 1. Effect of solvent polarity on the mode of fission of β-propiolactone by trimethyltin methoxide. Each two millimoles of β-propiolactone and trimethyltin methoxide in 1.00 ml of solvent (70° for 4 h).

It is clear from Table 1 that the amount of the acyl–oxygen bond fission decreases with the increasing polarity of the solvent. There is a fairly good linear relationship between the logarithms of the relative amount of two products and the Kirkwood parameter $(\varepsilon-1)/(2\varepsilon+1)$, shown in Fig. 1. This indicates that the transition state for the alkyl–oxygen bond fission has more dipolar character than that for the acyl–oxygen cleavage. We have previously shown[13] that the rate of the reaction between β-propiolactone and N-(trimethylsilyl)piperidine involving alkyl–oxygen bond fission is higher in polar media.

Since β-propiolactone is cleaved selectively through the acyl–oxygen bond fission in carbon tetrachloride a kinetic study for this main reaction was possible. Kinetic studies were carried out by determining the change of infrared frequency at 1842 cm^{-1}, which is characteristic of the β-lactone ring. Typical second order plots were obtained for the reaction between 0.100 mole/l each of β-propiolactone (β-PL) and trimethyltin methoxide. The rate constants for the initial stage [initial concentrations of trimethyltin methoxide $(C)_0$, were 0.150, 0.200 and 0.300 mole/l, respectively, ($[\beta\text{-PL}]_0=0.100$ mole/l)] were 4.6, 6.1 and $9.2\cdot10^{-4}$ sec^{-1}, respectively, indicating that the order with respect to trimethyltin methoxide is 0.96 ± 0.11. The reaction is thus of first order in each reactant. Second order rate constants obtained at five temperatures are summarized in Table 2.

TABLE 2

SECOND ORDER RATE CONSTANTS k_2, FOR THE ACYL–OXYGEN FISSION OF β-PROPIOLACTONE WITH TRIMETHYLTIN METHOXIDE IN CARBON TETRACHLORIDE[a]

Temp. (°C)	10^3k_2 ($l\cdot mole^{-1}\cdot sec^{-1}$)
48.0	1.13±0.10
55.0	2.14±0.11
60.0	3.43±0.07
65.0	4.78±0.13
67.0	6.14±0.06

[a] $[\beta\text{-PL}]_0=[Me_3SnOMe]_0=0.100$ mole/l.

From the Arrhenius plot for these rate constants the activation energy and entropy were found to be 19.3 kcal/mole and 12.1 $cal\cdot mol^{-1}\cdot degree^{-1}$, respectively. Since these activation parameters are reasonable for a normal S_N2 reaction, trimethyltin methoxide is suggested to behave as a nucleophilic reagent to the carbonyl oxygen atom in β-propiolactone.

The signal due to the trimethyltin group in the reaction mixture containing (I) and (II), was unexpectedly found as a singlet at τ 9.62 ppm, although independent (I) and (II) showed singlets at τ 9.63 and 9.50 ppm, respectively, which suggested the existence of an interaction between the trimethyltin groups in (I) and (II). To throw light on this possibility the NMR spectrum of the mixture of trimethyltin methoxide and authentic (II) was studied. The signals ascribed to the trimethyltin groups coalesce to a singlet at τ 9.57, which is broader than both of the original compounds. Interaction of the trimethyltin groups is thus confirmed. Similar interaction was found to occur for the system consisting of Me_3SnCl/Me_3SnOMe,

Me_3SnCl/Me_3SnSMe, Me_3SnBr/Me_3SnOMe, Me_3SnBr/Me_3SnSMe, and (II)/Me_3SnBr at room temperature in carbon tetrachloride.

EXPERIMENTAL

The infrared and NMR spectra were obtained, respectively, with a Nippon Bunko IR-S and a Japan Electron Optics C-60 type spectrometer in carbon tetrachloride.

Materials

Trimethyltin methoxide was prepared[14] by the methanolysis of trimethyltin in diethylamide. Recrystallization from n-hexane was performed for three times and dried under reduced pressure. β-Propiolactone was purified by distillation.

Methyl β-(trimethylstannyl)propionate. To methyl β-hydroxypropionate (0.5 g) obtained by the methanolysis of β-propiolactone[11], the same molar amounts of trimethyltin diethylamide was added gradually at 0°. The mixture was kept at room temperature for 1 h, and at 50° for 30 min. Methyl β-(trimethylstannyl)propionate (0.8 g) was obtained as distillation residue. (Found Sn, 44.26. $C_7H_{16}O_2Sn$ calcd.: Sn, 44.75%.) The carbonyl stretching frequency was shown at 1740 cm^{-1}. The NMR spectrum gave signals at τ 9.63 singlet with satellites due to ^{117}Sn and ^{119}Sn, 7.66 triplet (J 6.8 cps), 6.42 singlet, and 6.23 triplet.

The infrared and NMR spectrum of this authentic material was completely the same as those of the product obtained from trimethyltin methoxide and β-propiolactone in carbon tetrachloride, in which the product was formed through the acyl–oxygen bond fission predominantly.

Trimethyltin β-methoxypropionate. The equimolar mixture of β-methoxypropionic acid (1.0 g) and trimethyltin diethylamide reacted exothermally. After the removal of diethylamide, a white crystalline product was obtained in quantitative yield. M.p. 84.2° (recrystallized from n-hexane). (Found: C, 31.29; H, 6.03. $C_7H_{16}O_2Sn$ calcd.: C, 31.49; H, 6.04%.) The carbonyl stretching absorption due to trimethyltin carboxylate appeared at 1653 cm^{-1}. The NMR spectrum gave signals at τ 9.50 singlet with two satellite ascribed to ^{117}Sn and ^{119}Sn, 7.75 triplet (J 7.1 cps), 6.77 singlet, 6.56 triplet.

Determination of the product ratio (I)/(II)

Each 2.00 millimoles of β-propiolactone and trimethyltin methoxide was reacted at 70° for 4 h with 1.00 ml of solvent. After removal of the solvent under reduced pressure, carbon tetrachloride containing 2 vol% of tetramethylsilane as an internal standard for NMR measurement was added. From the relative intensity of the signal at τ 6.42 for (I) and at τ 6.77 for (II), the ratios of (I)/(II) were determined. The results are given in Table 1.

Kinetic study

Trimethyltin methoxide (1.00 millimole) was dissolved in carbon tetrachloride in a 10 ml measuring flask. One millimole of β-propiolactone was added by means of a microsyringe. The solution was divided into several ampoules filled with argon and sealed. These sealed ampoules were kept in the bath thermostatically controlled to ±0.3°. At appropriate times, an ampoule was broken and the concentration of remaining β-propiolactone was measured from the intensity of the absorption at 1842 cm^{-1}.

SUMMARY

The acyl–oxygen bond of β-propiolactone is preferentially cleaved by trimethyltin methoxide in non-polar media, but cleavage of the alkyl–oxygen bond also occurs in polar media. The plot of the logarithm of the ratio of acyl–oxygen to alkyl–oxygen cleavage against $(\varepsilon-1)/(2\varepsilon+1)$ shows a linear relationship. In carbon tetrachloride, in which predominantly acyl–oxygen bond cleavage takes place, the reaction shows second-order kinetics; the activation energy is 19 kcal/mole and the activation entropy is -12 $cal \cdot mole^{-1} \cdot degree^{-1}$.

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