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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS II. DUAL BEHAVIOR OF THE RING OPENING OF β-PROPIOLACTONE BY TRIMETHYLSILYL-, GERMYL- AND STANNYL DIETHYLAMINE.

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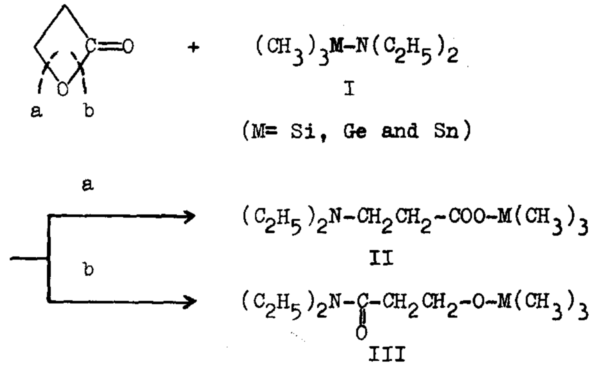
Two possible modes of ring openings can be considered for the reaction of β-propiolactone with trimethylmetal(IV) diethylamine I, as follows.

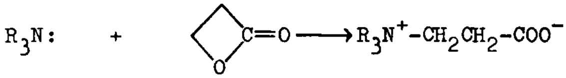


We found that trimethylsilyl diethylamine(I, M= Si) reacted with β-propiolactone at 80°C for 24 hours, giving exclusively the trimethylsilyl ester of N,N-diethyl-β-alanine (II, M= Si) through the course a. in 88% yield.[1] Proton magnetic resonance spectrum of the adduct showed a sharp methyl singlet of the trimethylsilyl group at 9.74τ, a methyl triplet at 8.98τ and complex multiplets due to three types of methylene proton between 7.2-7.9τ. The carbonyl stretching frequency was observed at 1720 cm^{-1}.

The reaction of trimethylgermyl diethylamine (I, M= Ge; 2.6 millimoles) with β-propiolactone(2.3 millimoles) was carried out in 0.2 ml of ethylene dichloride at 80°C for 6 hours. Distillation of the product gave a colorless and hydrolyzable liquid fraction boiling at 86.9-87.2°C/ 3mmHg in 67% yield. Infra-red spectrum of this adduct showed a strong carbonyl stretching frequency at 1682 cm^{-1} and no amide absorption was observed between 1600-1650 cm^{-1}. This adduct showed almost the same proton magnetic resonance spectrum as that of the trimethylsilyl ester of N,N-diethyl-β-alanine(II, M= Si), that is, a sharp singlet of the trimethylgermyl group at 9.60τ, a methyl triplet at 9.05τ and complex multiplets ascribed to methylene protons between 7.2-7.9τ. No signal was observed downfield from 7.0τ. A triplet due to a methylene proton adjacent to an oxygen atom would be expected in this region, if III(M= Ge) was formed. For instance, $^{n}Bu_3Ge\text{-}O\text{-}C\underline{H}_2\text{-}CH_3$ showed a quartet at 6.27τ. When this adduct was treated with hydrochloric acid dissolved in ether, the hydrochloride of N,N-diethyl-β-alanine was obtained quantitatively.

Therefore, it was concluded that in the case of trimethylgermyl diethylamine(I, M= Ge), β-propiolactone was attacked at the β-carbon atom(via. a.) to give the trimethylgermyl ester of N,N-diethyl-β-alanine(II, M= Ge) in the same manner as trimethylsilyl diethylamine(I, M= Si).

Gresham <u>et.al.</u>[2] reported that the alkyl-oxygen bond of β-propiolactone was broken by the nucleophilic attack of tertiary amines.



Therefore, the nucleophilic attack of the nitrogen atom in I (M= Si and Ge) might be important as in tertiary amines. This point of view is supported by the kinetic studies which will be reported later.

However, in the case of trimethylstannyl diethylamine (I, M= Sn), a quite different behavior was observed. When 10 millimoles of β-propiolactone were added to 12 millimoles of trimethylstannyl diethylamine, a violent exothermic reaction took place even at room temperature and reaction mixture turned into viscous liquid. The adduct was obtained in 95% yield after the removal of the excess trimethylstannyl diethylamine under reduced pressure. The adduct was purified by distilling at 85.0-87.0°C/ 0.04 mmHg in 50% yield. A strong carbonyl stretching frequency at 1640 cm^{-1} could be ascribed to a tertiary amide group, because $CH_3COOSn(CH_3)_3$ showed $\nu_{C=O}$ at 1655 cm^{-1}.

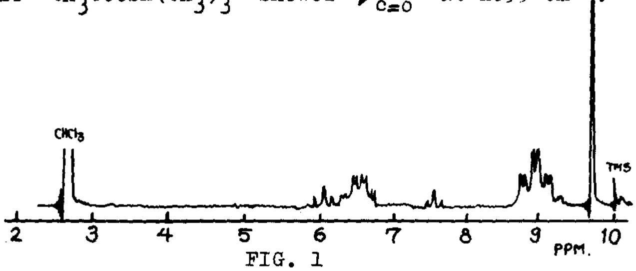
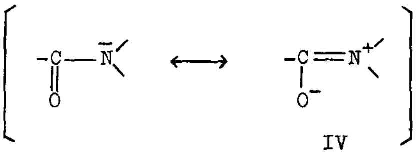


FIG. 1

NMR spectrum of N,N-diethyl-β-trimethylstannoxypropionamide (III, M= Sn) in $CHCl_3$ at 20°C.

Proton magnetic resonance spectrum of this adduct was quite different from that obtained in the case of trimethylsilyl and germyl ester of N,N-diethyl-β-alanine (II, M= Si and Ge) as shown in FIG. 1. A characteristic signal of an alkoxy proton was observed as a triplet at 6.22τ and well compared with that obtained in the case of $(CH_3)_3SnO\underline{CH_2}CH_3$ at 6.44τ. Any other signals could be explained from the structure of N,N-diethyl-β-trimethylstannoxypropionamide (III, M= Sn), that is, a singlet at 9.72τ was ascribed to the trimethylstannyl group, two triplets at 8.90 and 9.03τ to amide methyl protons, a triplet at 7.60τ to $-CO-\underline{CH_2}-$ and two quartets at 6.76 and 6.82τ to amide methylenes. The separation of the spectra od amide protons is well known for. that of several amides[3] and carbamates[4] and explained by a conception of the fixed internal rotation due to the following structure IV.



IV

Treatment of the adduct with hydrochloric acid caused a shift of the amide absorption from 1640 to 1620 cm^{-1}. N,N-Diethyl-β-hydrooxypropionamide prepared from diethylamine and β-propiolactone according to Gresham et.al.[2] showed an amide absorption at 1620 cm^{-1}.

Above results suggest that β-propiolactone was cleaved through the acyl-oxygen bond fission(via. b.) to give III (M= Sn). This different behavior of trimethylstannyl diethylamine (I, M= Sn) is interesting and may be explained by the tendency of either a coordination of carbonyl oxygen atom on the tin atom in I (M= Sn) or a nucleophilic attack of the nitrogen atom on the carbonyl carbon atom.

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