

Formation of *N*-Tributylstannyl-2-oxazolidone from $(\text{Bu}_3\text{Sn})_2\text{O}$ and 2-Chloroethyl Isocyanate

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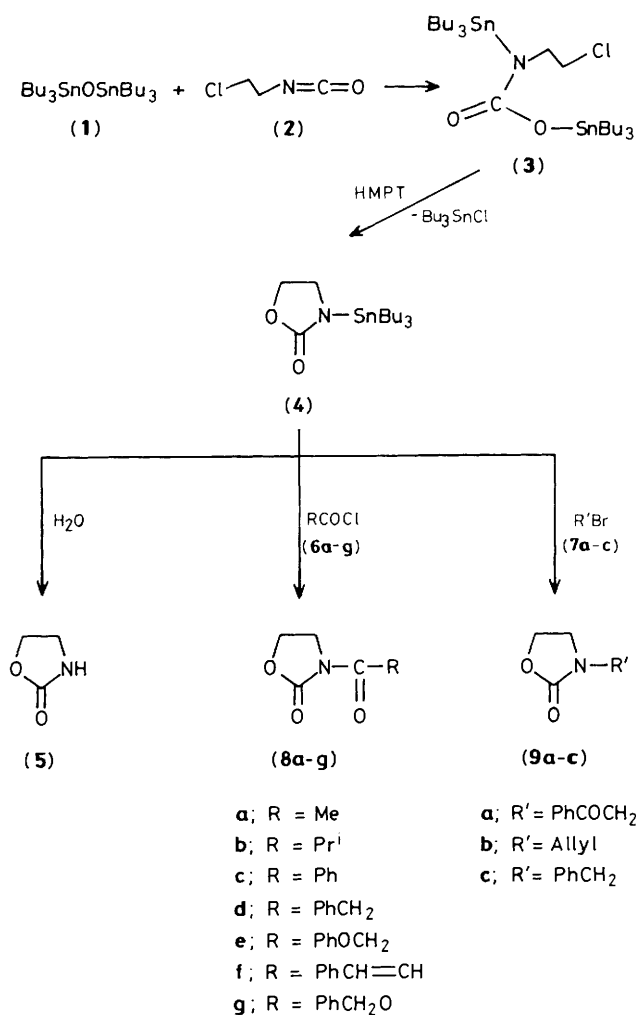
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N-Tributylstannyl-2-oxazolidone is formed from the reaction of $(\text{Bu}_3\text{Sn})_2\text{O}$ and 2-chloroethyl isocyanate in the presence of hexamethylphosphoric triamide, and reacts with electrophiles to give *N*-substituted 2-oxazolidones in good yields.

We have recently reported the use of organotin ω -halogenoalkoxides.¹ Owing to the high reactivity of the Sn–O bond and the affinity of the Sn atom towards the terminal halogen, a variety of five- and six-membered heterocyclic compounds were readily produced under mild conditions. We have explained the enhancement observed on adding Lewis bases to these cyclizations in terms of the co-ordination to the Sn atom. In connection with our interest in the use of this type of organotin ω -halogeno compound, we report here the formation and reactions of *N*-tributylstannyl-2-oxazolidone (**4**). Although *N*-trimethylsilyl-2-oxazolidone is widely used as a silylating agent,² the formation of the *N*-stannylated analogue has not been reported so far.

As shown in Scheme 1, (**4**) is readily formed from the reaction of $(\text{Bu}_3\text{Sn})_2\text{O}$ (**1**) and 2-chloroethyl isocyanate (**2**). A typical procedure is as follows. The isocyanate (**2**) (10 mmol)

was added slowly to (**1**) (10 mmol) under dry nitrogen; heat was evolved and the β -halogeno-*N*-stannyl carbamate (**3**) was formed,³ as confirmed by the appearance of an i.r. absorption band at 1600 cm^{-1} accompanied by the disappearance of the band due to the NCO group (2280 cm^{-1}). Next, hexamethylphosphoric triamide (HMPT) (4 ml) was added, and heating at 40°C for 1 h induced cyclization to form (**4**). I.r. spectra showed the appearance of a band at 1770 cm^{-1} (C=O). Furthermore, the reactions with electrophiles were carried out without isolating (**4**). Compound (**4**) is so reactive that it was readily hydrolysed during the usual work-up required for isolation, and 2-oxazolidone (**5**), which showed an i.r. band at 1720 cm^{-1} (C=O) was obtained quantitatively. Reactions of (**4**) with equimolar amounts of acid chlorides (**6a–g**) were complete at room temperature within 10 min, yielding the corresponding *N*-acyl-2-oxazolidones (**8a–g**) in high yields



Scheme 1

(86–100%). The products were isolated by column chromatography.†

The use of HMPT is essential. Otherwise, cyclization hardly occurred, and (8c) was obtained in only 5% yield. This important role of HMPT may be explained by its coordination to Sn in (3), which increases the basicity of the oxygen atom adjacent to Sn and accelerates the intramolecular alkylation.

When phenacyl, allyl, and benzyl bromides (7a–c) were used as electrophiles, although the reaction conditions (80 °C, 15 h) were not as mild as in the case of acid chlorides, the corresponding 2-oxazolidones (9a–c) were obtained (76, 81, and 60%, respectively). In general, the N-alkylation of 2-oxazolidones must be carried out in strong alkaline media.⁴ Thus activation of the nitrogen through stannylation is effective, and similar activation has also been reported for some heterocycles.⁵ In conclusion, therefore, our method has several advantages in terms of mild and neutral conditions, high yields of products, and operational convenience.

Received, 14th July 1986; Com. 968

References

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- 3 It has been reported that the Sn–O bond is easily inserted into isocyanate to give an N-stannyl carbamate: A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 1965, 6245.
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† Satisfactory elemental analyses and spectroscopic data were obtained for new product (8b), (8d), (8f), and (9a). Previous reports have appeared for compounds (8a), (8c), (8g), (9b), and (9c) (see *Chem. Rev.*, 1966, **66**, 197) and compound (8e) [*Chem. Abstr.*, 1978, **88** (25), 190655e].