

Dehydrochlorination of Hydroximoyl Chlorides by the Use of Vinyltins for Synthesis of Isoxazolines (Dihydrooxazoles)

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The reaction of hydroximoyl chlorides and vinyltin compounds afforded isoxazolines *via* dehydrochlorination and [3 + 2] dipolar cycloaddition.

In previous work, we have reported that organotin compounds such as bis(tributyl)tin oxide and tetraphenyltin are useful reagents for the generation of nitrile oxides from hydroximoyl chlorides *via* dehydrochlorination.¹ In particular, the fact that tetraphenyltin could be used for the reaction suggested that organotin compounds with relatively weak Sn–C bonds would react with the chlorinated derivatives of aldehyde oximes analogously. By considering the reported data on the relative ease of cleavage of various organic groups from tin,² vinylic tin compounds seemed to trap hydrogen chloride effectively. Furthermore, the vinyl moieties were expected to function as dipolarophiles. We now describe the results of our studies along these lines, in which vinyltins **2** are treated with hydroximoyl chlorides **1** for the preparations of isoxazolines **3** *via* a nitrile oxide intermediate.

The vinyltin derivatives **2** and allenyltributyltin **4** were prepared by the reactions of tin hydrides and alkynes *via* radical- or palladium-catalysed hydrostannation.^{3–5} To carry out the [3 + 2] dipolar cycloadditions, a solution of the chloride **1** and an equimolar amount of **2** in benzene was stirred at 60 °C for 5 h or overnight at room temperature. The desired product **3** was isolated by silica gel chromatography with chloroform as eluent. The reactions of **1** and the vinyltins

2 having a functional group which increased the charge separation of the unsaturated moiety proceeded efficiently and afforded the cyclization products **3**, and **5**, in moderate yields (Table 1). Attempts to control the regioselectivities of the cycloadditions by use of the regioisomeric vinyltins **2b** and **2c** were unsuccessful; the same isoxazoline derivative **3b** was

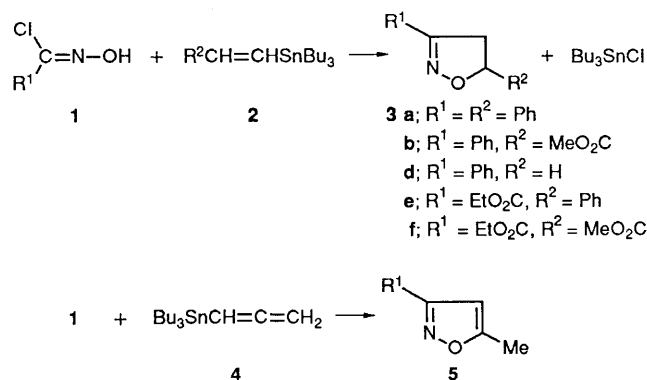


Table 1 Formation of isoxazolines **3**

R ¹ in 1	2 or analogue	Yield (%) of 3
Ph	2a , R ² = Ph	3a (80)
Ph	2b , R ² = MeO ₂ C	3b (76)
Ph	2c , CH ₂ =C(CO ₂ Me)SnBu ₃	3b (63)
Ph	2d , R ² = H	3d (11)
EtO ₂ C	2a , R ² = Ph	3e (75)
EtO ₂ C	2b , R ² = MeO ₂ C	3f (66)
Ph	4 , Bu ₃ SnCH=C=CH ₂	5 (61)
Ph	6 , (<i>E</i>)-Ph ₃ SnCH=CHCO ₂ Me	3b (65)

obtained in analogous yields. Tributylvinyltin **2d** was obtained in analogous yields. Tributylvinyltin **2d** and allenyltributyltin **1**, which may be regarded as synthons of ethene and propyne, respectively, were also used; the isoxazoline **3d** was obtained in poor yield from **2d**. However, 3-phenyl-5-methylisoxazole **5**, which we think is formed through isomerization of the corresponding isoxazoline having an exomethylene group,⁶ was obtained in reasonable yield from **4**. In addition, the triphenylvinyltin derivative **6**, in which one of the phenyl groups seemed to be substituted by halogen more readily than the vinyl moiety,² was also examined as a dipolarophile.

However, the formation of the isoxazoline having a chlorodiphenyltin substituent was not observed. The reaction of **1** and **6** gave the isoxazoline **3b** and triphenyltin chloride.

Thus, vinyltins were demonstrated to act as both dehydrochlorination reagents and dipolarophiles. The results show that the latter role was apparent only after the cleavage of the vinylic moiety from tin, *i.e.* the cycloaddition reactions proceeded preferentially between the nitrile oxides and the tin-free vinylic compounds.

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References

- O. Moriya, Y. Urata and T. Endo, *J. Chem. Soc., Chem. Commun.*, 1991, 17.
- R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 1960, **60**, 459.
- R. C. Poller, *The Chemistry of Organotin Compounds*, Logos Press, London, 1970, pp. 105–130.
- H. Miyake and K. Yamamura, *Chem. Lett.*, 1989, 981.
- Y. Ueno and M. Okawara, *J. Am. Chem. Soc.*, 1979, **101**, 1893.
- C. Caristi and M. Gattuso, *J. Chem. Soc., Perkin Trans. 1*, 1974, 629.