

Preliminary communication

THE UNEXPECTED FORMATION OF  $\alpha$ -ADDUCTS IN THE  
 HYDROSTANNATION OF TRIALKYLVINYLTIN COMPOUNDS

ERIC J. BULTEN\* and HENK A. BUDDING

*Institute for Organic Chemistry TNO, Utrecht (The Netherlands)*

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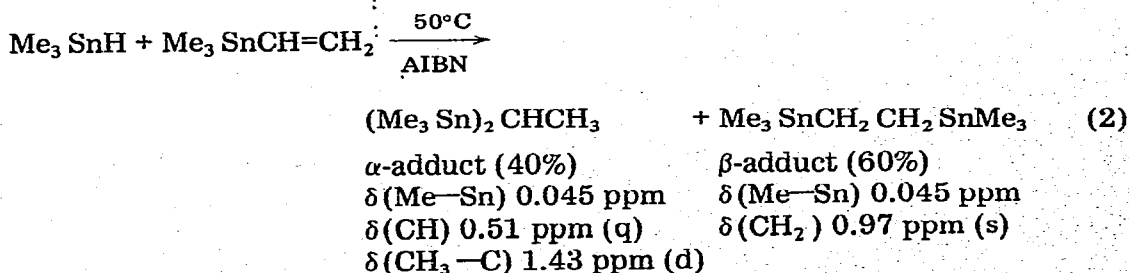
Summary

Hydrostannation of trialkylvinyltin compounds,  $R_3 SnCH=CH_2$  ( $R = Me, Et$ ) with trialkyltin hydrides,  $R_3 SnH$  ( $R = Me, Et$ ) gives both  $\alpha$ - and  $\beta$ -adducts, rather than  $\beta$ -adducts exclusively, as expected.

As a starting material for studies of the synthesis of stannacycloalkanes [1] by reaction 1 a sample of the unknown compound 1,2-bis(trimethylstannyl)- $R_3 Sn(CH_2)_n SnR_3 \xrightarrow{\Delta} R_4 Sn + R_2 Sn(CH_2)_n$  (1)

ethane was required. In the light of considerable knowledge of the hydrostannation of terminal olefins [2,3] reaction of trimethyltin hydride with trimethylvinyltin under free radical conditions was expected to give exclusively the  $\beta$ -adduct,  $Me_3 SnCH_2 CH_2 SnMe_3$ . However, we find that reaction of the neat products at  $50^\circ C$  in the presence of 2 mol percent of azobisisobutyronitrile (AIBN) gives a mixture of the  $\alpha$ - and the  $\beta$ -adduct in the ratio 2/3.

In the absence of AIBN reaction proceeds considerably slower, but the product composition is not changed ( $\alpha$ -adduct/ $\beta$ -adduct 2:3).

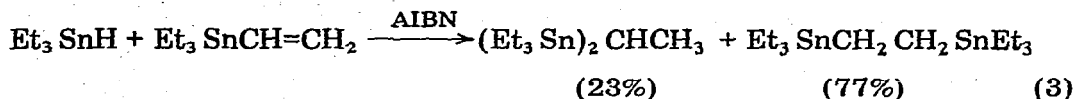


The pure  $\alpha$ - and  $\beta$ -adduct were isolated by preparative GLC and identified by  $^1H$  NMR spectrometry. Degradation of the isomer mixture with bromine

\*To whom correspondence should be addressed.

in carbon tetrachloride solution gave the expected products, 1,1-dibromoethane and 1,2-dibromoethane, in the ratio 43:57.

Reaction of triethyltin hydride with triethylvinyltin catalyzed by AIBN has been previously reported to give exclusively the  $\beta$ -adduct [3,4]. We found, however, that the latter reaction also gives an isomer mixture, which according to bromine degradation and subsequent GLC analysis consists of 23% of the  $\alpha$ -adduct and 77% of the  $\beta$ -adduct.



By means of  $^1\text{H}$  NMR spectrometry as well as bromine cleavage we have confirmed the exclusive formation of the  $\beta$ -adduct in the hydrostannation of triphenylvinyltin with triphenyltin hydride, as reported previously by Henry and Noltes [5] (cf. ref. 6).

The reaction of acrylonitrile with trialkyltin hydrides represents the only published example of non-terminal hydrostannation of terminal olefins [7]. However, in that case a polar mechanism was found to be operative in the formation of the  $\alpha$ -adduct, which is not formed at all in the presence of AIBN [7]. The formation of  $\alpha$ -adduct in the hydrostannation of trialkylvinyltin compounds with trialkyltin hydride under free radical conditions is rather unexpected and will be further investigated.

## References

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