

## STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXIX\*. MECHANISM OF THE HYDROSTANNATION OF STRONGLY ELECTROPHILIC CARBONYL COMPOUNDS\*\*

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### SUMMARY

The mechanism of the hydrostannation of strongly electrophilic carbonyl compounds has been studied. From the kinetics, and the solvent and substituent effects, it appears that the addition reaction proceeds by nucleophilic attack of the hydride hydrogen on carbon. Further aspects of this and secondary reactions are discussed.

### INTRODUCTION

Organotin hydrides add exothermally across the carbon-oxygen double bond of chloral, pentafluorobenzaldehyde and 2,2,2-trifluoroacetophenone, affording alkoxytin compounds:



As discussed in the preceding paper<sup>1</sup> the first formed 1 : 1 adducts may react with one of the reactants, yielding among others 1 : 2 adducts. In the present paper the results of a study of the mechanism of hydrostannation reaction (1) are presented.

### RESULTS AND DISCUSSION

In Figs. 1-3 the results of a kinetic study of the hydrostannation of 2,2,2-trifluoroacetophenone are presented. Fig. 1 clearly shows that the rate of reaction increases strongly with increasing polarity of the medium. As Fig. 2 shows, the rate of reaction increases in the order  $\text{Ph}_3\text{SnH} \ll \text{Bu}_3\text{SnH} < \text{Me}_3\text{SnH} < \text{Et}_3\text{SnH}$ . Neither phenoxy nor acetophenone affects the rate of reaction.

Autocatalytic effects, as found<sup>2,3</sup> in the hydrostannation of isocyanates and salicylaldehyde, were not observed.

Similar results were obtained in the hydrostannation of pentafluorobenzaldehyde. The reaction is much faster in butyronitrile than in cyclohexane; the rate of reaction increases in the order  $\text{Ph}_3\text{SnH} \ll \text{Bu}_3\text{SnH} < \text{Me}_3\text{SnH} < \text{Et}_3\text{SnH}$ . Phenoxy as well as benzaldehyde have a negligible effect on the rate. From preliminary experi-

\* For Part XXVIII see ref. 1.

\*\* Taken from the Ph.D. thesis of one of us (A.J.L.).

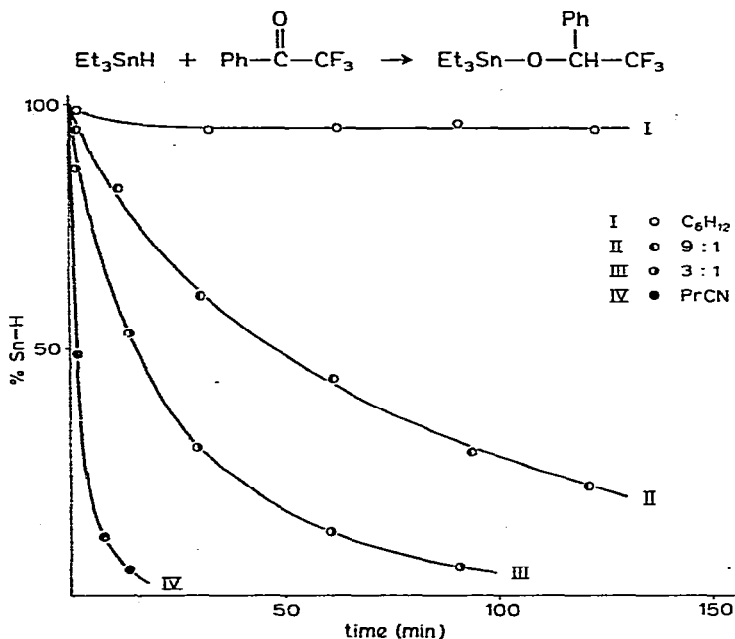


Fig. 1. Reaction of triethyltin hydride ( $0.15 \text{ mole}\cdot\text{l}^{-1}$ ) with 2,2,2-trifluoroacetophenone ( $0.45 \text{ mole}\cdot\text{l}^{-1}$ ) in cyclohexane ( $\text{C}_6\text{H}_{12}$ ), butyronitrile (PrCN) and mixtures of these solvents at  $20.0^\circ$ . 9:1 = mixture of 9 volumes of cyclohexane and 1 volume of butyronitrile; 3:1 = mixture of 3 volumes of cyclohexane and 1 volume of butyronitrile.

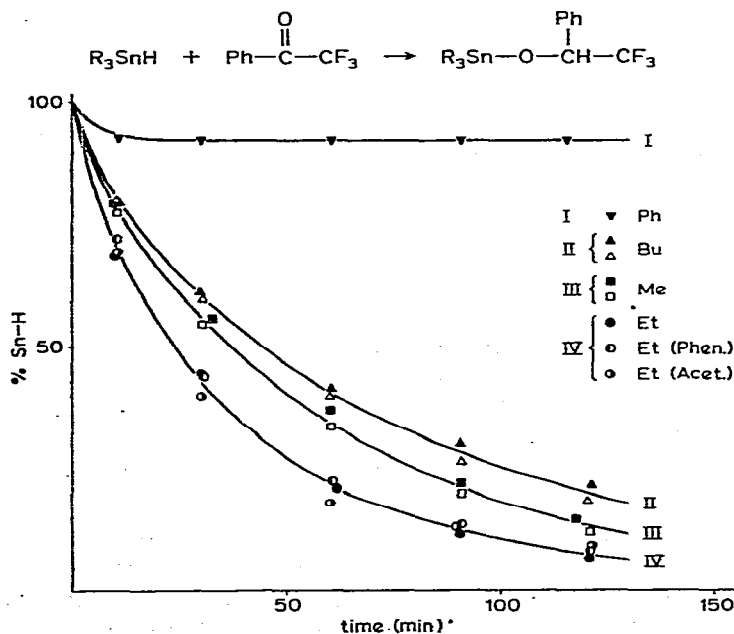


Fig. 2. Reaction of triorganotin hydrides ( $0.15 \text{ mole}\cdot\text{l}^{-1}$ ) with 2,2,2-trifluoroacetophenone ( $0.45 \text{ mole}\cdot\text{l}^{-1}$ ) in a mixture of 3 volumes of cyclohexane and 1 volume of butyronitrile at  $20.0^\circ$ . Phen. = 3.2 mole % of phenoxyl; Acet. =  $0.30 \text{ mole}\cdot\text{l}^{-1}$  acetophenone.

ments it appeared that samples taken from a freshly distilled portion of the aldehyde were less reactive than samples taken from a portion which had been allowed to stand for some time. Since it must be expected that in the latter case traces of acid had been formed, it seemed likely that the reaction is subject to acid catalysis. This view was corroborated by the increase of the reaction rate, observed when catalytic amounts of benzoic acid were added. Under the conditions employed the hydride did not react with benzoic acid, as appeared from a separate experiment.

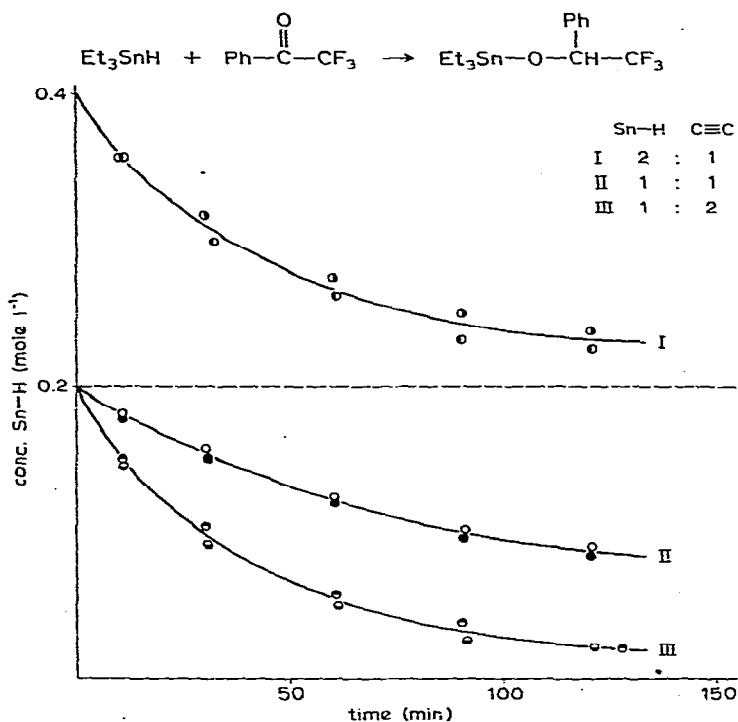


Fig. 3. Reaction of triethyltin hydride with 2,2,2-trifluoroacetophenone in a 2 : 1, 1 : 1 and 1 : 2 ratio in a mixture of 3 volumes of cyclohexane and 1 volume of butyronitrile at 20.0°. Initial concentrations of triethyltin hydride: 0.40, 0.20 and 0.20 mole·l<sup>-1</sup>, respectively; initial concentrations of 2,2,2-trifluoroacetophenone: 0.20, 0.20 and 0.40 mole·l<sup>-1</sup>, respectively. All experiments were run in duplicate.

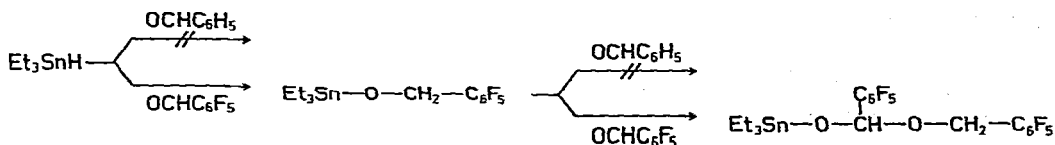
As Fig. 3 indicates, the reaction follows second-order kinetics and is first order in each reactant. Consequently, the results are the same as those described previously for the ionic hydrostannation of C=C<sup>4</sup>, C≡C<sup>5</sup>, C=N<sup>6</sup> and C=S<sup>6</sup> bonds, viz.:

- the rate of reaction increases with increasing polarity of the solvent;
- electron-releasing substituents at tin\* and electron-withdrawing substituents attached to the carbonyl group accelerate the reaction;
- the free radical scavenger phenoxyl does not affect the rate of reaction.

Thus it seems likely that the hydrostannation of these electrophilic carbonyl compounds again proceeds by a nucleophilic attack of the hydride hydrogen on carbon:

\* The reversed order Et<sub>3</sub>SnH > Bu<sub>3</sub>SnH obviously arises from steric effects.





The attack could be either by oxygen of the undissociated 1 : 1 adduct or by oxygen of the anion  $\text{HCR}_2-\text{O}^-$ . This anion originates either from the dissociation of the 1 : 1 adduct or from the primary step of the hydrostannation reaction. This implies that the 1 : 1 adduct is not necessarily a precursor of the 1 : 2 adduct.

#### EXPERIMENTAL

The kinetic experiments were carried out by measuring the intensity of the Sn-H absorption band around  $1800\text{ cm}^{-1}$  in the IR spectrum as described in previous papers<sup>5,6</sup>. These spectra, which were run by Mrs. G. E. E. Sniijders-Woldringh and Miss H. Alberda, were recorded using a Perkin-Elmer spectrophotometer type Infra-cord 137 and a Grubb Parsons Spectromaster.

*Addition of triethyltin hydride to 2,2,2-trifluoroacetophenone at 20.0° in cyclohexane, butyronitrile and mixtures of these solvents (Fig. 1)*

Initial concentrations:  $0.15\text{ mole}\cdot\text{l}^{-1}$  triethyltin hydride and  $0.45\text{ mole}\cdot\text{l}^{-1}$  2,2,2-trifluoroacetophenone.

Relative rate constants:  $< 0.02$  (in cyclohexane), 1 (in a mixture of 9 volumes of cyclohexane and 1 volume of butyronitrile), 3.1 (in a mixture of 3 volumes of cyclohexane and 1 volume of butyronitrile),  $> 25$  (in butyronitrile).

The adduct ( $0.075\text{ mole}\cdot\text{l}^{-1}$ ) did not influence the rate of reaction (in cyclohexane).

*Addition of triorganotin hydrides to 2,2,2-trifluoroacetophenone at 20.0° in a mixture of 3 volumes of cyclohexane and 1 volume of butyronitrile (Fig. 2)*

Initial concentrations:  $0.15\text{ mole}\cdot\text{l}^{-1}$  triorganotin hydride ( $\text{R}_3\text{SnH}$ ) and  $0.45\text{ mole}\cdot\text{l}^{-1}$  2,2,2-trifluoroacetophenone. Substituents at tin:  $\text{R}=\text{Ph}$ ,  $\text{R}=\text{Me}$ ,  $\text{R}=\text{Et}$ ,  $\text{R}=\text{Et}$  in the presence of 3.2 mole % of phenoxy,  $\text{R}=\text{Et}$  in the presence of  $0.30\text{ mole}\cdot\text{l}^{-1}$  acetophenone,  $\text{R}=\text{Bu}$ .

Relative rate constants:  $< 0.02$  ( $\text{R}=\text{Ph}$ ), 0.8 ( $\text{R}=\text{Bu}$ ), 1 ( $\text{R}=\text{Me}$ ) and 1.5 ( $\text{R}=\text{Et}$ ). Neither phenoxy, nor acetophenone affected the rate of reaction.

*Addition of triethyltin hydride to 2,2,2-trifluoroacetophenone in a 2 : 1, 1 : 1 and 1 : 2 ratio at 20.0° in a mixture of 3 volumes of cyclohexane and 1 volume of butyronitrile (Fig. 3)*

Initial concentrations:  $0.40\text{ mole}\cdot\text{l}^{-1}$  triethyltin hydride and  $0.20\text{ mole}\cdot\text{l}^{-1}$  2,2,2-trifluoroacetophenone;  $0.20\text{ mole}\cdot\text{l}^{-1}$  triethyltin hydride and  $0.20\text{ mole}\cdot\text{l}^{-1}$  2,2,2-trifluoroacetophenone;  $0.20\text{ mole}\cdot\text{l}^{-1}$  triethyltin hydride and  $0.40\text{ mole}\cdot\text{l}^{-1}$  2,2,2-trifluoroacetophenone.

Half-life periods (from 0% to 50% conversion): 35 min (2 : 1), 91 min (1 : 1) and 30 min (1 : 2).

*Addition of triethyltin hydride to pentafluorobenzaldehyde at 20.0° in butyronitrile and cyclohexane*

Initial concentrations: 0.30 mole·l<sup>-1</sup> triethyltin hydride and 0.90 mole·l<sup>-1</sup> pentafluorobenzaldehyde. Solvents and catalysts: cyclohexane, butyronitrile, butyronitrile in the presence of 1.6 mole % of phenoxyl, butyronitrile in the presence of 0.30 mole·l<sup>-1</sup> benzaldehyde, butyronitrile in the presence of 1.3 mole %\* of benzoic acid, butyronitrile in the presence of 2.6 mole %\* of benzoic acid.

Relative rate constants: < 0.1 (in cyclohexane), 1 (in butyronitrile), ~1.5 (id. with 1.3 mole % of benzoic acid) and ~2 (id. with 2.6 mole % of benzoic acid). Neither phenoxyl nor benzaldehyde did appreciably affect the reaction rate (relative rate constants: ~1).

In a separate experiment the reaction of triethyltin hydride (0.30 mole·l<sup>-1</sup>) with benzoic acid (0.30 mole·l<sup>-1</sup>) in butyronitrile was followed by means of IR spectroscopy. No reaction had occurred at all after 125 min at 20°.

*Addition of triorganotin hydrides to pentafluorobenzaldehyde at 20.0° in butyronitrile*

Initial concentrations: 0.30 mole·l<sup>-1</sup> triorganotin hydride (R<sub>3</sub>SnH) and 0.90 mole·l<sup>-1</sup> pentafluorobenzaldehyde. Substituents at tin: R = Ph, R = Me, R = Et, R = Bu.

Relative rate constants: < 0.1 (R = Ph), 0.85 (R = Bu), 1 (R = Me) and ~1.2 (R = Et).

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#### REFERENCES

- 1 A. J. LEUSINK, H. A. BUDDING AND J. W. MARSMAN, *J. Organometal. Chem.*, 13 (1968) 155.
- 2 A. J. LEUSINK, Ph.D. thesis, State University of Utrecht, The Netherlands, 1966.
- 3 W. P. NEUMANN AND E. HEYMANN, *Justus Liebigs Ann. Chem.*, 683 (1965) 11.
- 4 A. J. LEUSINK AND J. G. NOLTES, *Tetrahedron Lett.*, (1966) 335.
- 5 A. J. LEUSINK, H. A. BUDDING AND W. DRENTH, *J. Organometal. Chem.*, 9 (1967) 295.
- 6 A. J. LEUSINK, H. A. BUDDING AND J. G. NOLTES, *Rec. Trav. Chim. Pays-Bas*, 85 (1966) 151.
- 7 W. R. CULLEN AND G. E. STYAN, *Inorg. Chem.*, 4 (1965) 1437.
- 8 A. G. DAVIES AND W. R. SYMES, *J. Chem. Soc., C*, (1967) 1009.

\* Based on the initial amount of aldehyde.