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STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXVI*. FREE RADICAL *trans*-ADDITION OF ORGANOTIN HYDRIDES TO CARBON–CARBON TRIPLE BONDS**

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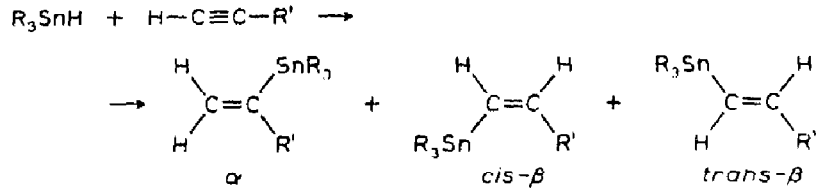
INTRODUCTION

Hydrostannation of unsaturated bonds can proceed by an ionic as well as by a free radical chain mechanism. Hydrostannation of ethynes containing exclusively strongly electron-withdrawing substituents has been shown[1,2] to proceed mainly or exclusively by an ionic process. Mechanistic details of this ionic reaction, leading to α-adducts in the case of monosubstituted electrophilic ethynes, have been presented in part XXV of this series[2]. The β-adducts which also may be formed in additions to monosubstituted electrophilic ethynes, were regarded[1] to originate from a free radical reaction.



This paper deals with the mechanistic aspects of the free radical reaction. The hydrostannation of ethynes containing electron-releasing substituents, which proceeds exclusively by such a mechanism, will be discussed as an example. As will be shown below, the hydrostannation of disubstituted ethynes containing both an electron-withdrawing and an electron-releasing substituent also belongs to this class. Hydrostannations of monosubstituted ethynes containing a weakly electron-withdrawing substituent have not been investigated as such. However, the results of the present studies indicate that also these additions will proceed mainly by the free radical mechanism.

RESULTS AND DISCUSSION

Influence of the polarity of the solvent and of free radical scavengers and initiators

In Figs. 1 and 2 the result of experiments on the addition of trimethyltin hydride to ethyl 1-propynecarboxylate as followed by GLC in butyronitrile ($\varepsilon = 20.3$)

* For Part XXV see ref. 2.
** Taken from the Ph. D. thesis of one of us (A.J.L.).

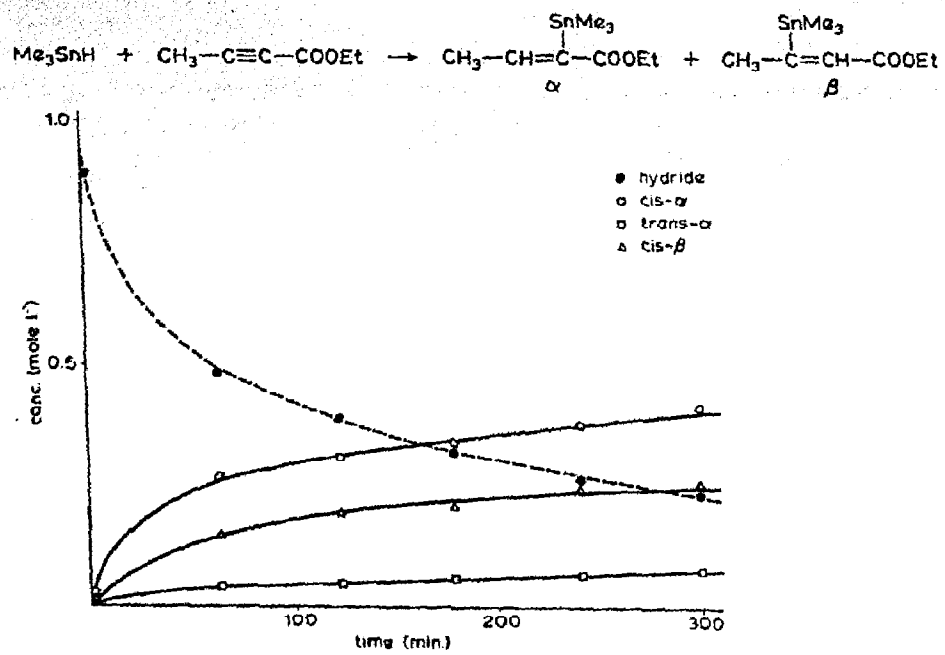


Fig. 1. Reaction of trimethyltin hydride (0.940 mole·l^{-1}) with ethyl 1-propynecarboxylate (2.000 mole·l^{-1}) in butyronitrile at 49.9°.

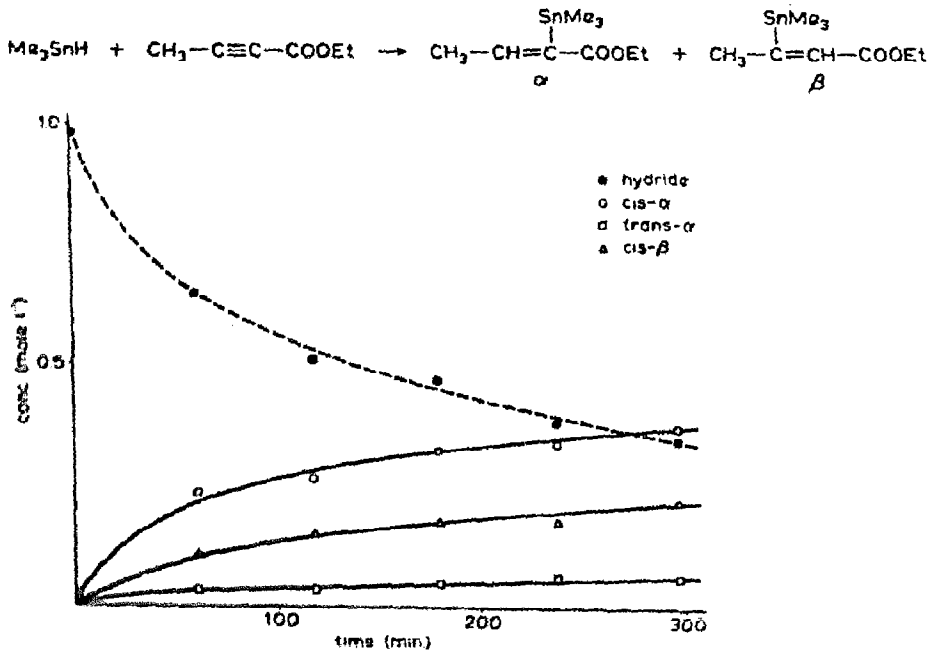


Fig. 2. Reaction of trimethyltin hydride (1.000 mole·l^{-1}) with ethyl 1-propynecarboxylate (1.936 mole·l^{-1}) in decane at 49.9°.

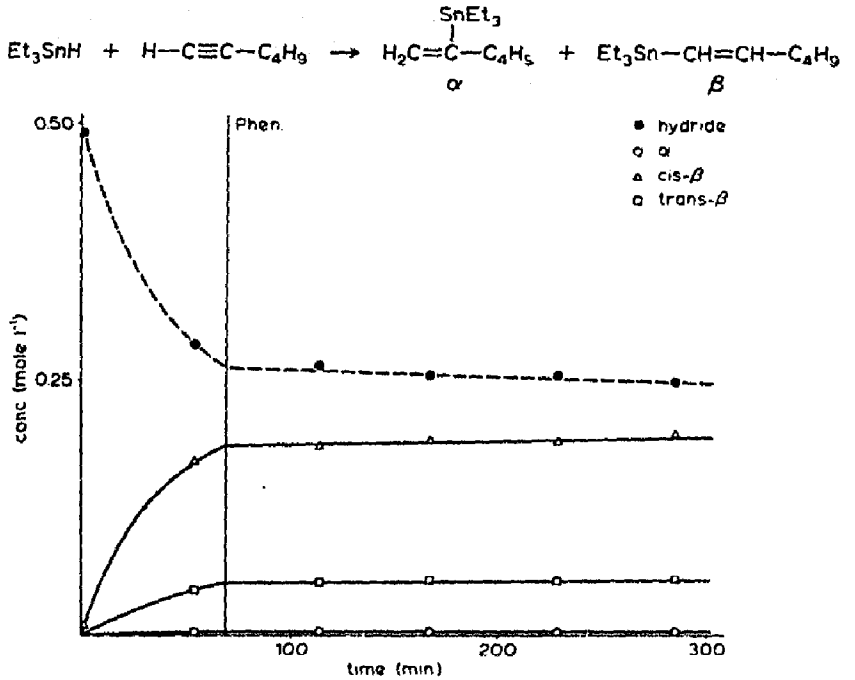


Fig. 3. Reaction of triethyltin hydride (0.500 mole·l^{-1}) with 1-hexyne (0.950 mole·l^{-1}) in o-xylene at 49.9°. Addition of 2.4 mole % of phenoxyl after 69 min.

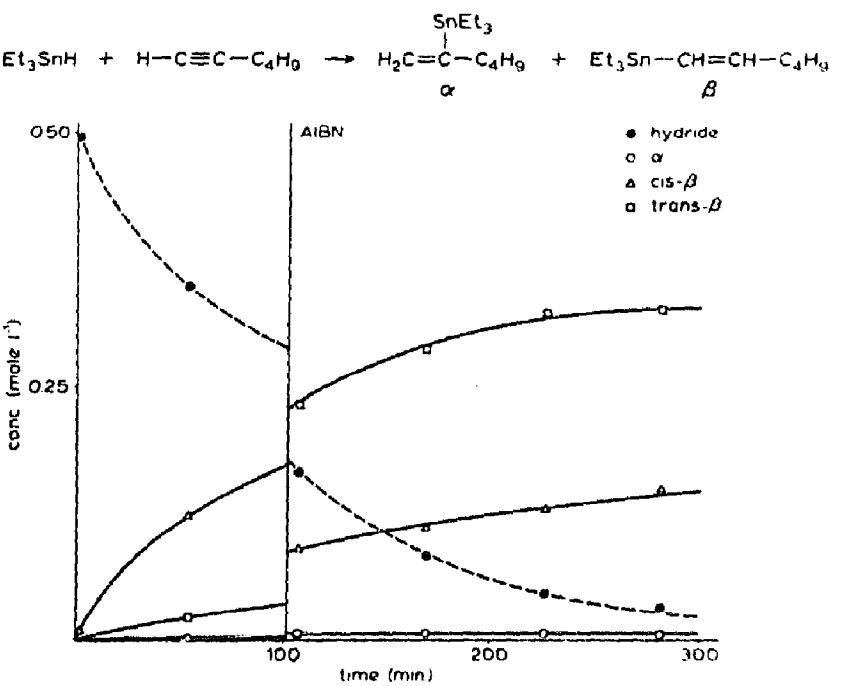


Fig. 4. Reaction of triethyltin hydride (0.500 mole·l^{-1}) with 1-hexyne (0.915 mole·l^{-1}) in o-xylene at 49.9°. Addition of 2.4 mole % of AIBN after 102 min.

and decane ($\varepsilon = 1.99$), respectively, are shown. In this type of reaction considerable amounts of the α-adducts were formed. Although the rate of formation of both α- and β-adducts is not exactly the same in these solvents, it is obvious that the polarity of the solvent is not of great importance for the reaction rate.

Similar results were obtained[3] in the hydrostannation of 1-hexyne. In this case mainly the *cis*-β- and *trans*-β-adducts were formed, together with a very small amount of the α-adduct. Analogous to the results obtained with ethyl 1-propynecarboxylate the rates of formation of the α-adduct as well as that of the β-adducts appeared to be practically solvent-independent.

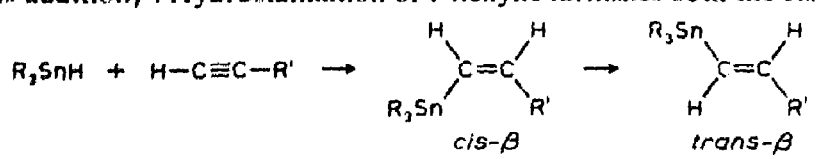
Figs. 3 and 4 demonstrate the tremendous influence of the free radical scavenger phenoxyl* and of the free radical initiator AIBN** on the hydrostannation of 1-hexyne. As follows from Fig. 3 addition of phenoxyl stops the hydrostannation almost completely. It appears from Fig. 4 that AIBN causes a strong and sudden increase in the total amount of adducts, whereupon the reaction resumes its former rate. The sudden rise in the total amount of products, in particular of the *trans*-β-adduct, is accompanied by a sudden drop in the amount of the *cis*-β-adduct. This phenomenon will be discussed more fully in a following paper[4]. The same course of events, *viz.* total inhibition by phenoxyl and initiation by AIBN, was observed[3] in the hydrostannation of ethyl 1-propynecarboxylate.

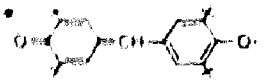
The negligible influence of the polarity of the solvent on the rate of formation of both the α- and β-adducts in the present cases makes an ionic mechanism highly improbable. The effects observed upon addition of AIBN prove that the reaction *can* proceed *via* a free radical mechanism. That a radical mechanism is operative also in the absence of the initiator is proven by the effects observed upon addition of phenoxyl.

Similar results were obtained by Neumann and Sommer[5] in the addition of triethyltin hydride to phenylethyne in the absence of solvents. The structure of the 1 : 1 adducts was not studied by these authors, but it has been reported by Fulton[6] that the hydrostannation of this acetylenic compound in the absence of solvents leads exclusively to the β-adducts. The experiments described in a preceding paper[7] show that most probably in this case very small amounts of the α-adduct are formed as well.

Stereochemistry of the free radical addition reaction

In the absence of solvents the free radical addition reaction proceeds by a *trans*-addition. This has been proven by Fulton[6] in the case of phenylethyne. Essentially the same results were obtained in the present studies. For example, hydrostannation of ethoxyethyne yields almost exclusively the *cis*-β-adduct (occurrence of *trans*-addition)[7]. Hydrostannation of 1-hexyne furnishes both the *cis*-β- and *trans*-





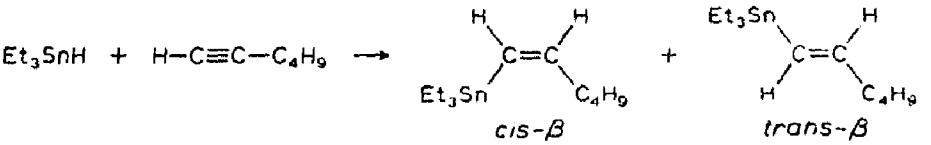
** azobisisobutyronitrile.

β-adducts, but during the addition the ratio *cis*-β/*trans*-β decreases considerably, indicating that the *cis*-β-adduct is the primary product and that the *trans*-β-adduct is formed by a subsequent rearrangement of the *cis*-β-adduct[7]. A similar rearrangement occurs during the addition of trimethyltin hydride to ethyl 1-propynecarboxylate[8]. In this case the ratio *cis*-α/*trans*-α* decreases whereas the *cis*-β-adduct obviously does not isomerize at all (*cf.* ref. 4).

The same course of events is observed in the presence of both polar and apolar solvents. Addition of trimethyltin hydride to methyl ethynecarboxylate and to cyanoethyne afforded, in addition to the α-adducts, exclusively the *cis*-β-adducts[1,3]. In the addition of triethyltin hydride to 1-hexyne the ratio *cis*-β/*trans*-β decreases steadily during the addition (Table 1). Similarly, the ratio *cis*-α/*trans*-α decreases

TABLE 1

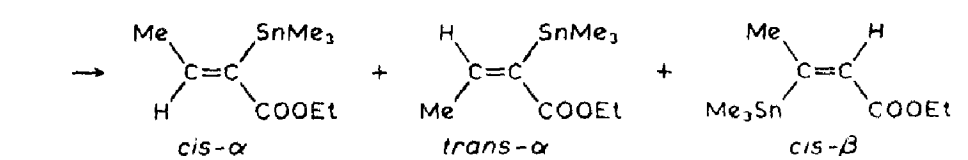
REACTION OF TRIETHYLTIN HYDRIDE WITH 1-HEXYNE IN *o*-XYLENE: RATIO *cis*-β/*trans*-β AS A FUNCTION OF THE PERCENTAGE OF CONVERSION OF THE HYDRIDE



Conversion of Et_3SnH (%)	*Ratio cis-β/trans-β*
2.0	>10
20.5	7.7
28.0	6.5
37.5	5.0
46.5	3.8
57.5	3.1

TABLE 2

REACTION OF TRIMETHYLTIN HYDRIDE WITH ETHYL 1-PROPYNECARBOXYLATE IN BUTYRONITRILE: RATIOS α/β AND *cis*-α/*trans*-α AS A FUNCTION OF THE PERCENTAGE OF CONVERSION OF THE HYDRIDE



Conversion of Me_3SnH (%)	*Ratio α/β*	*Ratio cis-α/trans-α*
5.0	2.0	>10
48.5	2.1	6.8
58.5	1.8	6.5
65.5	1.9	5.8
77.5	1.9	5.4

* The denotations *cis* and *trans* refer to the relation of the organotin substituent to the non-hydrogen substituent attached to the other ethylenic carbon atom. Thus, the *trans*-α-adduct from trimethyltin hydride and ethyl 1-propynecarboxylate is ethyl α-trimethylstannyl-*cis*-crotonate (see also Table 2)

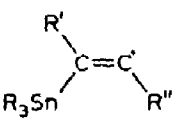
during the addition of trimethyltin hydride to ethyl 1-propynecarboxylate (Table 2). In the latter case the ratio total-α/*cis*-β remains almost constant (approximately 1.9), whereas the ratio *cis*-α/*cis*-β decreases from 1.9 to 1.6. This is in accord with the view that both types of *cis*-adducts are formed by a similar mechanism, and that the *cis*-α-adduct partly rearranges to the *trans*-α-adduct.

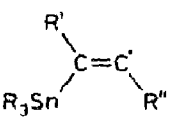
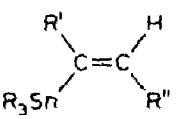
Thus, in the free radical addition reaction, both in the absence and in the presence of solvents, a *trans*-mechanism is operative (formation of *cis*-adducts). Any *trans*-adduct formed arises from an isomerisation of the primary *cis*-adduct. This stereochemical path is in conformity with the frontier-electron theory of Fukui[9].

Mechanism of the free radical addition reaction

Although the general nature of the hydrostannations under discussion has now been established, no exact picture exists regarding their overall mechanism. A free radical chain mechanism as shown below is in accord with the characteristics of the free radical hydrostannation (compare also refs. 10 and 11):

Initiation: $R_3SnH + X\cdot \xrightarrow{k_1} R_3Sn\cdot + XH$ (1)

Propagation: $R_3Sn\cdot + R'-C\equiv C-R'' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$  (2)

 $+ R_3SnH \xrightarrow{k_3}$  $+ R_3Sn\cdot$ (3)

In the case of monosubstituted ethynes (R' = H) β-adducts are formed almost exclusively, since terminal attack of the organotin radical* leads to secondary radicals [R_3Sn–CH=C·–R''] which are more stable than the alternative primary ones [·CH=C-(SnR_3)R''].

Which of the two steps of the propagation reaction plays the major part is not known at this moment. If $k_{-2} \ll k_3 \cdot [R_3SnH]$ step (2) is rate-determing; if $k_{-2} \gg k_3 \cdot [R_3SnH]$ step (3) is rate-determining. As discussed previously[3] step (2) may be rate-determining in the free radical addition to methyl ethynecarboxylate. On the other hand, it was shown[3,4] for additions to the carbon–carbon double bond of some ethenyltin compounds that $k_2 \geq k_3 \cdot [R_3SnH]$. These observations suggest that in the free radical hydrostannation of carbon–carbon unsaturated bonds either one of the propagation steps (2) and (3), or both these steps are rate-determing, depending on the nature of the reactants.

EXPERIMENTAL

Gas chromatographic analyses, which were performed by Miss G. G. de Haan, were carried out following the same procedures as described before[2,3].

* Recently the existence of triorganotin radicals has been demonstrated by means of electron spin resonance spectroscopy[12].

ACKNOWLEDGEMENT

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SUMMARY

Hydrostannation of ethynes containing exclusively an electron-releasing substituent, or both an electron-withdrawing and an electron-releasing substituent, have been shown to proceed by a free radical *trans*-addition. The mechanistic aspects of this reaction are discussed.

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