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STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXVII*. ISOMERIZATION OF THE PRIMARY *trans*-ADDITION PRODUCTS FORMED IN THE HYDROSTANNATION OF ETHYNES**

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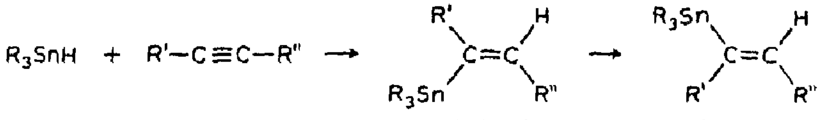
INTRODUCTION

In previous papers[1-3] we have shown that the hydrostannation of mono- and disubstituted ethynes proceeds either by an ionic *trans*-mechanism or by a free radical *trans*-mechanism, resulting in the formation of *cis*-adducts (I).



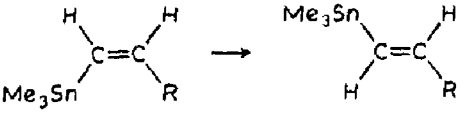
I (*cis*) II (*trans*)

In the present paper the isomerization of the primary *cis*-adducts (I) into the *trans*-adducts (II), which often are found to be present in hydrostannation mixtures[4-6], will be discussed.

RESULTS AND DISCUSSION

Nature of the isomerization reaction

The rearrangement of the *cis*- into the *trans*-adducts was found to proceed under the influence of a triorganotin radical ($R_3Sn^{\cdot}$). Fulton[7] reported that the *cis*-β-adduct (III, R = Ph) from trimethyltin hydride and phenylethyne did not isomerize thermally but yielded the *trans*-β-isomer (IV, R = Ph) when heated in the presence of trimethyltin hydride***. Similarly, Seyferth and Vaughan[8] reported that the *cis*-β-adduct (III, R = Me) from trimethyltin hydride and propyne did not rearrange thermally or in the presence of either AIBN or benzoyl peroxide, but did so upon



III (*cis*-β) IV (*trans*-β)

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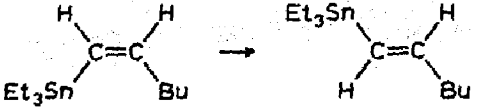
* For Part XXVI see ref. 3.

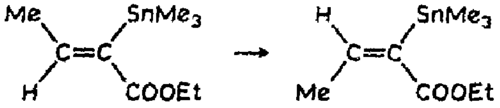
** Taken from the Ph. D. thesis of one of us (A.J.L.).

*** Analogous isomerizations under the influence of trimethyllead hydride were observed[9] with *cis*-β-adducts formed in the hydroplumbation of ethynes.

ultraviolet irradiation. That in fact an organotin radical is involved in the isomerization of both the α- and the β-adducts has been proven in our studies. In dilute solution the rearrangement of the *cis*-β-trimethyltin hydride adducts from methyl ethynecarboxylate (III, R = COOMe) and from cyanoethyne (III, R = CN) occurs only in the simultaneous presence of the hydride and of AIBN[1,5]. During the hydrostannation of 1-hexyne and ethyl 1-propynecarboxylate the rate of isomerization of the

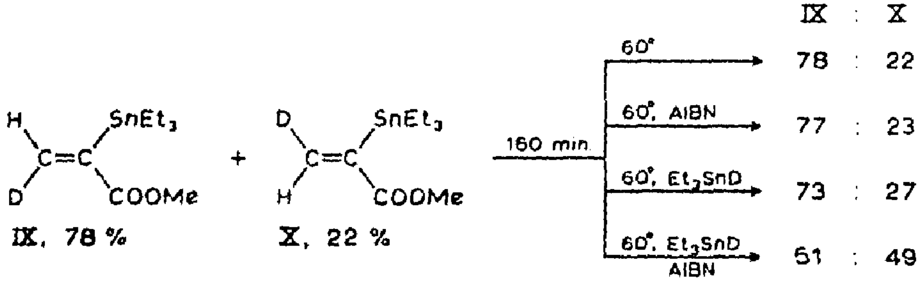


V (*cis*-β) VI (*trans*-β)



VII (*cis*-α) VIII (*trans*-α)

cis-β- (V) and of the *cis*-α-adduct (VII), respectively, is increased largely upon addition of AIBN[3,5]. The isomerization stops completely upon addition of phenoxyl[3,5]. For example, in the hydrostannation of ethyl 1-propynecarboxylate the ratio *cis*-α/*trans*-α remains constant (*cis*-α/*trans*-α = 14) following the addition of phenoxyl; in the absence of catalysts this ratio decreases during the reaction from > 10 to 5.4; upon addition of AIBN a value of 3.8 is reached. Conclusive evidence for the indispensability of an organotin radical in these isomerization reactions was obtained from a study of the isomerization of the *cis*-α-adduct from trimethyltin deuteride and methyl ethynecarboxylate. This adduct (IX) rearranged neither thermally nor in the presence of AIBN; in the presence of triethyltin deuteride small amounts of the *trans*-α-adduct (X) were formed. However, complete isomerization to the 1 : 1 equilibrium mixture occurred in the simultaneous presence of AIBN and the organotin deuteride.



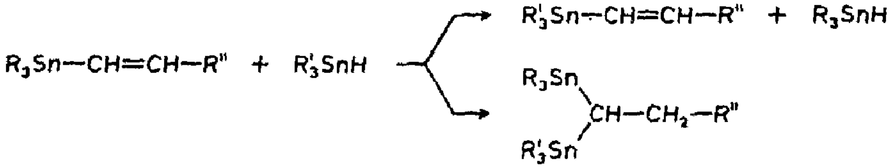
Mechanism of the isomerization reaction

Information about the mechanism of the isomerization reaction was obtained from experiments in which an organotin hydride R'_3SnH was brought into reaction with a 1 : 1 adduct $R_3Sn{-}CH{=}CH{-}R''$. The rates of formation of the several compounds formed by exchange, isomerisation and hydrostannation were followed by means of GLC.

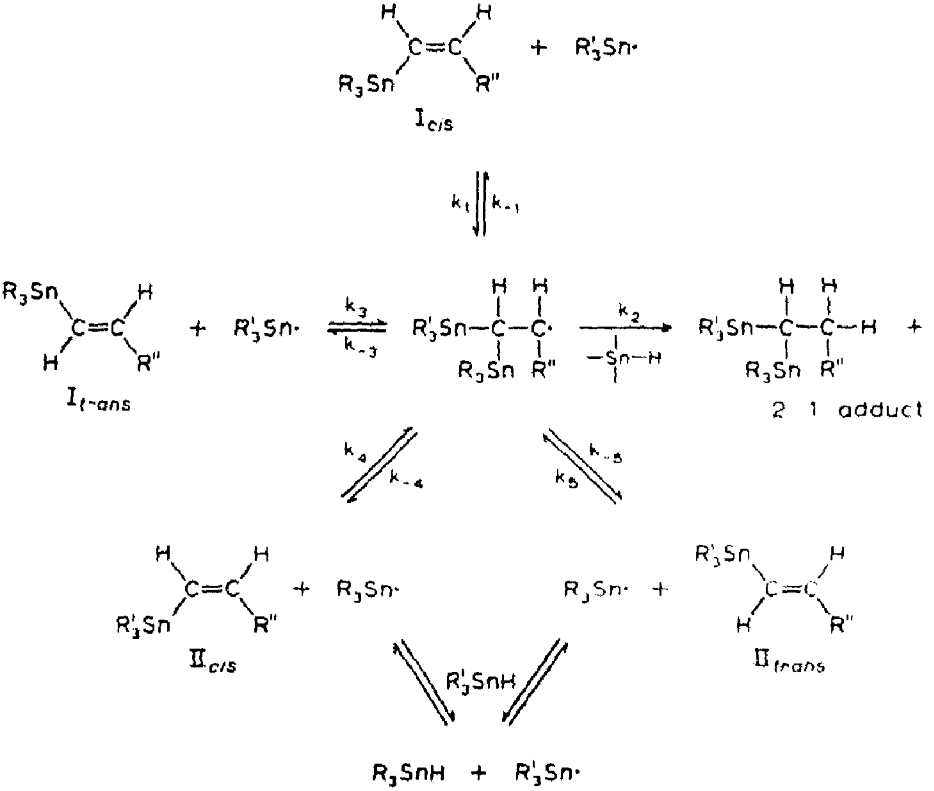
In the reaction of the hydride with the β-adducts from ethoxyethyne (R″ = OEt), in addition to isomerization, mainly exchange was observed:

$$R_3Sn{-}CH{=}CH{-}R'' + R'_3SnH \longrightarrow R'_3Sn{-}CH{=}CH{-}R'' + R_3SnH$$

Similarly, exchange occurred in the reaction of the hydride with the β-adducts from 1-hexyne (R″ = Bu). With the β-adducts from methyl ethynecarboxylate (R″ = COOMe) mainly exchange and hydrostannation were observed:



From the experimental data (initiation by AIBN and inhibition by phenoxyl) it appeared that both these exchange reactions and hydrostannations are free radical reactions. In the scheme presented below some of the several reactions which may occur, are depicted*:



In the initial stage of reaction compound I_{cis} with R″ = OEt is transformed almost exclusively to the II_{cis}-adduct. In this case the 2 : 1 adduct is not formed. Thus, $k_{-4} > k_{-3} \gg k_2 \cdot [\mathrm{SnH}]$. Again, hydrostannation was not observed for R″ = Bu and consequently $k_2 \cdot [\mathrm{SnH}]$ is very small with respect to k_{-n}. For R″ = COOMe $k_2 \cdot [\mathrm{SnH}] \approx k_{-4} > k_{-3}$. This is in agreement with previous observations that, even in the presence of free radical generators, addition to a non-terminal carbon–carbon double bond can only be realized if this bond is sufficiently activated. In the examples

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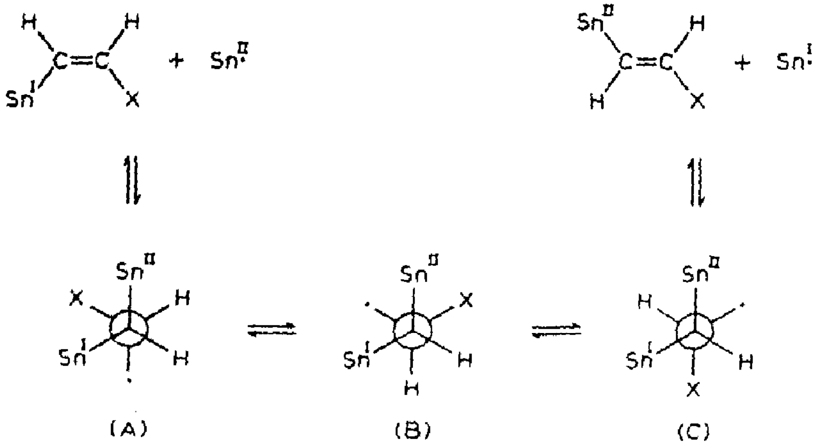
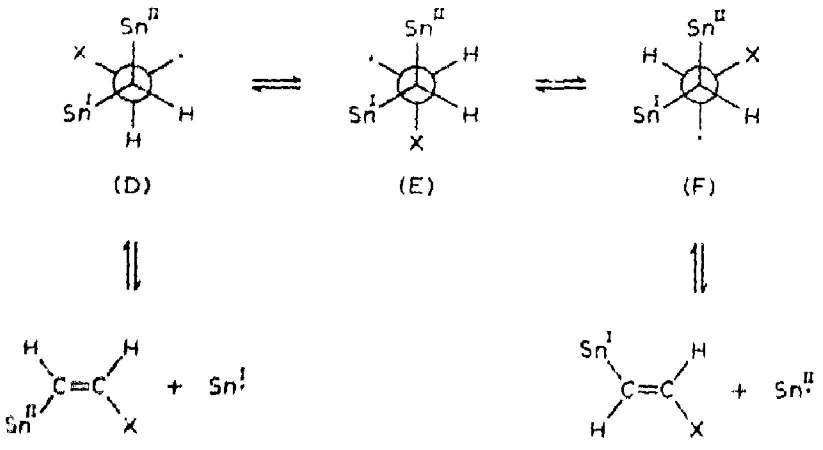
* Quite recently Neumann[10], without reference to our earlier work[5], proposed a similar reversible attack of an organotin radical on a carbon–carbon double bond as shown in this scheme.

described above k_{-4} will be of the same order as k_{-1}, thus $k_2 \cdot [\text{SnH}] \leq k_{-1}$. These facts show that in the hydrostannation of carbon–carbon double bonds hydrogen transfer may be a kinetically important step in the propagation reaction. In the case of non-activated carbon–carbon double bonds hydrogen transfer apparently is too slow for hydrostannation to occur.

The observation that in the exchange reactions involving adducts from ethoxyethyne and methyl ethynecarboxylate the I_{cis}-adducts are converted mainly into the II_{cis}-adducts (k_{-4} is much larger than k_{-3} and k_{-5}) points to a preference for certain conformational positions of the organotin groups in the free radical intermediate. The various staggered conformers of this intermediate are shown below. In this scheme it is assumed that the intermediate is formed by *trans*-addition and that the radical centre has the tetrahedral configuration which is capable of quick inversion. According to the principle of microscopic reversibility it is to be expected that the stereochemistry of the elimination reaction is also *trans*:



and the inverted structures:

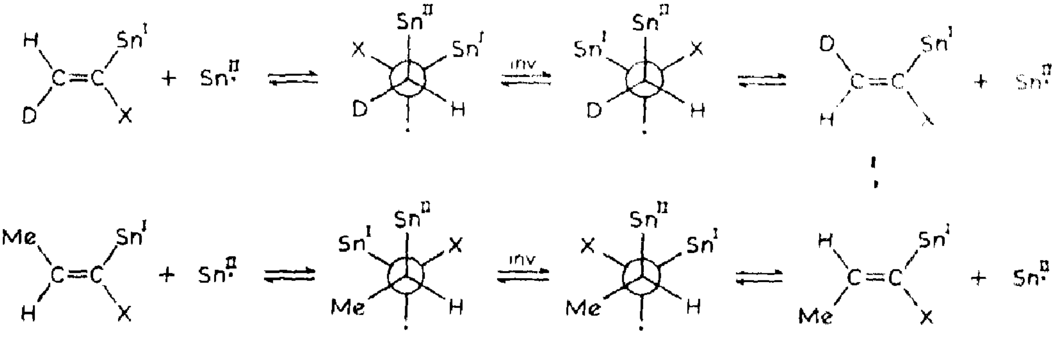


($X = \text{COOR, OEt, C}_4\text{H}_9$)

It appears from this scheme that the conformers (A) and (D) will yield *cis*-adducts, whereas conformers (C) and (F) will yield *trans*-adducts. Because *cis*-adducts are formed preferentially, and assuming that the rate of formation of the products will depend mainly upon the concentrations of the conformers, it must be concluded that (A) and (D) are present in higher concentrations than (C) and (F). Apparently, a favourable interaction between the tin atoms and the group X (COOMe, OEt) predominates over the opposing effect of a larger steric hindrance*. Interactions of a comparable kind have been observed in hydrolysis reactions of esters of the type $R_3MCH_2CH_2COOR'$ with M=Si, Ge and Sn[11].

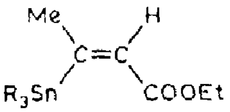
At the same time this mechanism accounts for the fact that in the free radical hydrostannation of methyl ethynecarboxylate and ethoxyethyne mainly the *cis-β*-adducts are obtained. The primarily formed *cis-β*-adducts do not rearrange readily during the hydrostannation since isomerization must proceed *via* the less favoured conformers (C) and (F). On the other hand, the *cis-β*-adduct formed in the hydrostannation of 1-hexyne is easily converted into the *trans-β*-adduct. Since in this case ($X=C_4H_9$) no attractive interaction with the tin atoms can occur the sterically less hindered conformers (C) and (F) of the free radical intermediate are favoured.

The isomerisation of the α-adduct (IX) from triethyltin deuteride and methyl ethynecarboxylate and of the α-adduct (VII) from trimethyltin hydride and ethyl 1-propynecarboxylate described before is likely to proceed *via* a similar mechanism. Since, as has been shown[4] for methyl propiolate, the second organotin group becomes attached to the β-carbon atom, these isomerisations must proceed *via* inversion at the radical centre of the intermediate:



(X = COOR)

The *cis-β*-adduct (XI) from ethyl 1-propynecarboxylate does not isomerize at all which may be due to steric hindrance. In addition, for the same reasons as discussed above, the intermediate, if formed at all, will yield preferentially the original adduct.



XI (*cis-β*)

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* The impeded formation of the *trans*-adducts may also be explained by a retardation of the rate of elimination as a result of attractive interaction between the leaving tin radical and the polar group X. In conformers (C) and (F) these forces are larger than in conformers (A) and (D).

EXPERIMENTAL

Essentially the same techniques as described in previous papers[2,6] were employed. Gas chromatographic analyses were performed by Miss G. G. de Haan. NMR spectra (60 and 100 MHz) were run by Mr. M. J. A. de Bie (Laboratory of Organic Chemistry, State University of Utrecht*) and Miss L. Veldstra.

As examples of the procedures followed two experiments have been described below.

Reaction of trimethyltin hydride with cis-β-triethylstannylethoxyethene as followed by means of gas chromatography

A mixture of 2.0 mmoles of trimethyltin hydride and 2.0 mmoles of *cis*-β-triethylstannylethoxyethene was kept at 50.3° for several hours. At appropriate time intervals 1 μl samples were taken from the reaction mixture and analyzed by means of gas chromatography [F & M Gas Chromatograph Model 500; 12′ stainless steel column $\frac{1}{4}$″ OD packed with 20% Silicone Oil DC 710 on Diatoport WAW 60–80 mesh; temperature of injection port: 200°; column temperature: 13 min at 140° and 15 min at 200°; block temperature: 225°; bridge current: 150 mA; carrier gas (helium) velocity: 65 ml/min]. The amounts of adducts present were calculated from the peak areas and molar responses, which had been determined by calibration with pure samples of the products.

During the first stages of the reaction the β-adducts were found to be present in ratios of *cis*-β-Me$_3$Sn : *trans*-β-Me$_3$Sn ≧ 10 : 1 and *cis*-β-Et$_3$Sn : *trans*-β-Et$_3$Sn ≧ 30 : 1. After 4 h approximately 25% of the triethyltin adducts were converted into trimethyltin products. At the same time triethyltin hydride had been formed, while the ratios *cis*-β : *trans*-β changed considerably in favour of the *trans*-β-products: *cis*-β-Me$_3$Sn : *trans*-β-Me$_3$Sn = 2.5 : 1, *cis*-β-Et$_3$Sn : *trans*-β-Et$_3$Sn = 7 : 1. The overall rate was slightly increased by the addition of 3 mole % of AIBN (after 260 min). After 6 h approximately 40% of the trimethyltin product had been formed, while the ratios had changed to *cis*-β-Me$_3$Sn : *trans*-β-Me$_3$Sn = 1.8 : 1 and *cis*-β-Et$_3$Sn : *trans*-β-Et$_3$Sn = 3.8 : 1.

After standing at room temperature for another 46 h the NMR spectrum of the resulting mixture revealed the presence of the products in the ratio *cis*-β-Me$_3$Sn : *trans*-β-Me$_3$Sn : *cis*-β-Et$_3$Sn : *trans*-β-Et$_3$Sn = approximately 25 : 20 : 35 : 20.

In a second experiment 3 mole % of phenoxyl was added after 47 min, which resulted in the complete inhibition of all conversions. The ratios of the products were found to be *cis*-β-Me$_3$Sn : *trans*-β-Me$_3$Sn = 3.2 : 1 and *cis*-β-Et$_3$Sn : *trans*-β-Et$_3$Sn = 8.4 : 1.

Under similar conditions total inhibition was observed of the reaction between triethyltin hydride and an equimolecular amount of *cis*-β-trimethylstannylethoxyethene at 50.5° when 3 mole % of phenoxyl was added within 30 sec after the start of the reaction.

Isomerization of methyl α-triethylstannylacrylate-cis-β-d in cyclohexane at 60°

In four NMR tubes (a, b, c and d, respectively) were introduced under nitrogen

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[*] The authors are much indebted to Professor J. F. Arens of this laboratory for making available the 60 MHz NMR spectrometer.

400 μl of cyclohexane and 100 μl of a mixture of 78 % of methyl α-triethylstannylacrylate-*cis*-*β*-*d* (IX) and 22 % of methyl α-triethylstannylacrylate-*trans*-*β*-*d* (X). To tubes b, c and d were added: 3.2 mg of AIBN (b), 25 μl of triethyltin deuteride (c) and 3.2 mg of AIBN together with 25 μl of triethyltin deuteride (d). The tubes were heated at 60° for 160 min and then cooled to room temperature. The NMR spectra (Varian Associates A-60 NMR spectrometer) of the resulting mixtures revealed the presence of compounds (IX) and (X) in ratios of 78 : 22 (a), 77 : 23 (b), 73 : 27 (c) and 51 : 49 (d).

ACKNOWLEDGEMENT

The authors are much indebted to Professor G. J. M. VAN DER KERK and to Dr. J. G. NOLTES for helpful discussions.

SUMMARY

The isomerization of the primary *trans*-addition products formed in the hydrostannation of ethynes has been shown to proceed under the influence of organotin radicals. Attack of such radicals on the carbon–carbon double bond produces an ethyl radical containing two organotin groups. Elimination of one of the organotin moieties as a radical may result in the formation of the isomerized product. The course of the latter step is determined by several factors. One of these seems to be a preference for those conformers of the free radical intermediate in which both tin atoms at the *β*-carbon atom are in *gauche*-position with respect to the polar substituent at the α-carbon atom.

At the same time these studies reveal that in hydrostannations of certain carbon–carbon double bonds the hydrogen transfer, following the reversible attack of an organotin radical, is the rate-determining step in the propagation reaction.

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