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STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXV*. NUCLEOPHILIC *trans*-ADDITION OF ORGANOTIN HYDRIDES TO CARBON–CARBON TRIPLE BONDS**,***.

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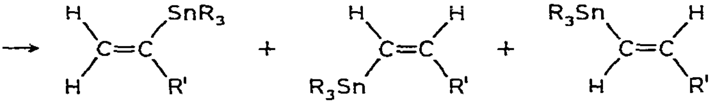
INTRODUCTION

In previous communications[1-4] the structures of the products of addition of organotin monohydrides to mono- and disubstituted ethynes were described and a mechanism of their formation was proposed. In the case of monosubstituted ethynes both α- and β-adducts were found to be present:

$$R_3SnH + H{-}C{\equiv}C{-}R' \longrightarrow$$



α cis-β trans-β

The α-adduct, apart from small amounts which must be expected in a free radical reaction, is formed in an ionic reaction. The *cis*-β-adduct is formed in a free radical reaction[6], whereas the *trans*-β-adduct is the result of isomerization of the *cis*-β-adduct[6].

Appreciable amounts of α-adducts are formed when the substituent R′ is strongly electron-withdrawing, *e.g.* with CN and COOR″. The rate of their formation is not influenced by the presence of radical inhibitors or of radical initiators[3,5], but the rate strongly depends on the polarity of the solvent system. Similar results were obtained in the hydrostannation of ethynes containing two strongly electron-withdrawing substituents attached to the triple bond[5].

In this paper additional data supporting the ionic addition mechanism are presented. In a subsequent paper[6] the free radical addition mechanism will be discussed.

RESULTS

In the first reports on organotin hydride additions it was suggested that in additions to ethenes a four-centre mechanism might be operative since hydroboration

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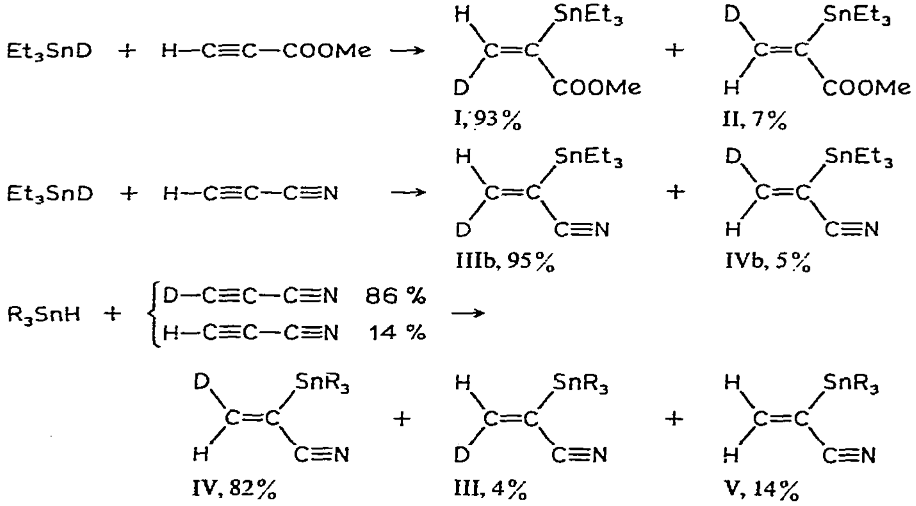
[*] Part XXIV: see ref. 4.

[**] A preliminary communication of this work has appeared in print[3].

[***] Taken from the Ph.D. thesis[5] of one of us (A.J.L.).

reactions had been found to proceed via this mechanism. In the ionic formation of the hydrostannation adducts a four-centre transition state in which bond-breaking and bond-making occur simultaneously, evidently is not involved, since such a mechanism does not account for the considerable solvent effects observed. Further evidence for the non-occurrence of a four-centre mechanism was derived from stereochemical data.

As has been shown previously[2,4] hydrostannation of diethyl ethynedicarboxylate in the absence of solvents yielded almost exclusively the *trans*-addition products. Corresponding results (in the absence of solvents) were obtained with methyl ethynecarboxylate and cyanoethyne, as appeared from experiments with deuterated compounds, *viz.*:



(IIIa)-(Va), R = Me; (IIIb)-(Vb), R = Et; (IIIc)-(Vc), R = Bu

Structural assignments were based on similar considerations as applied before[2,4] (differential shielding and ^{117,119}Sn–H coupling constants in the NMR spectra).

The isomers (II), (IVb) and (IIIa)-(IIIc) when present in small amounts in the reaction mixtures, most probably arise from a secondary rearrangement of the primary adducts, brought about by organotin radicals. A more detailed discussion of these and similar isomerizations will be given in a subsequent paper[6].

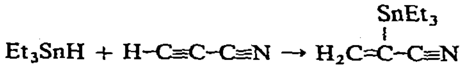
Essentially the same results were obtained in the presence of solvents. The stereochemistry of the following ionic hydrostannation reactions was investigated:

(*a*) Et_3SnD (0.30 mole·l^{-1}) with H–C≡C–C≡N (0.60 mole·l^{-1}) in butyronitrile and in methanol;

(*b*) Et_3SnH (0.10 mole·l^{-1}) with EtOOC–C≡C–COOEt (0.13 mole·l^{-1}) in butyronitrile and in cyclohexane;

(*c*) Et_3SnH (0.15 mole·l^{-1}) and Me_3SnH (0.27 mole·l^{-1}) with N≡C–C≡C–C≡N (0.22 and 0.40 mole·l^{-1}, respectively) in butyronitrile and in cyclohexane.

In each of these cases exclusive or almost exclusive *trans*-addition (>95%) occurred as appeared from NMR spectroscopy. Thus, in the ionic addition reaction, both in the absence and in the presence of the solvents used, a *trans*-mechanism is operative.



$$Et_3SnH + H{-}C{\equiv}C{-}C{\equiv}N \rightarrow H_2C{=}\overset{SnEt_3}{C}{-}C{\equiv}N$$

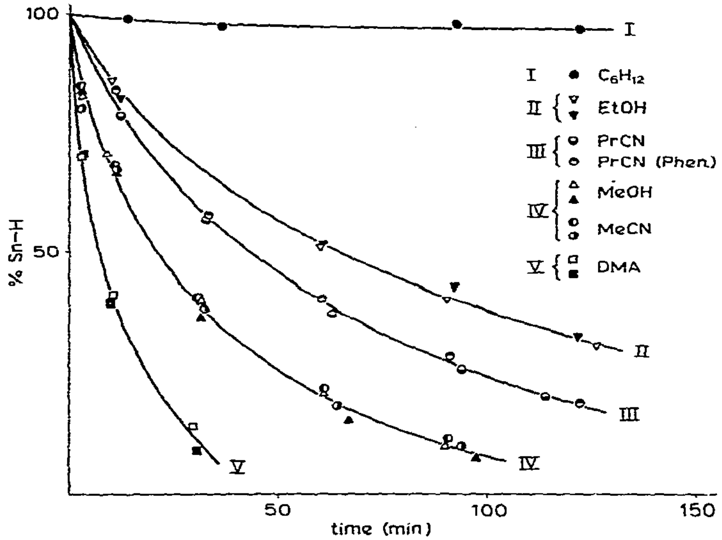


Fig. 1. Reaction of triethyltin hydride (0.29 mole·l^{-1}) with cyanoethyne (0.60 mole·l^{-1}) at 20.0° in cyclohexane (C_6H_{12}, ε 2.02), ethanol (EtOH, ε 24.2), butyronitrile (PrCN, ε 20.3), methanol (MeOH, ε 32.6), acetonitrile (MeCN, ε 37.5) and N,N-dimethylacetamide (DMA, ε 37.8). Phen. = 2.8 mole % of phenoxyl.

The influence of the polarity of the solvent is illustrated by Fig. 1, in which the conversion of triethyltin hydride in its reaction with cyanoethyne is plotted against time*. The progress of the addition was followed by measuring the intensity of the Sn–H stretching vibration in the infrared absorption spectrum. The rate of formation of the α-adduct, which is formed almost exclusively, increases in the solvent sequence

$$C_6H_{12} \ll C_2H_5OH < C_3H_7CN < CH_3OH \approx CH_3CN < CH_3CON(CH_3)_2$$

The dielectric constants of these solvents increase in approximately the same order: 2.02, 24.2, 20.3, 32.6, 37.5 and 37.8.

Quantitative data of the solvent effect expressed as a ratio of rate constants ($k_{\text{butyronitrile}}/k_{\text{apolar}}$) are given in Table 1. The ratio of rate constants in butyronitrile and in an apolar solvent like decane, extrapolated to zero concentration of the reagents, is in the order of a hundred or more. Exceptions are the additions to diethyl ethynedicarboxylate.

The influence of the substituents on tin on the rate of addition is illustrated by Fig 2*. The conversion of tin hydride was again followed by measuring the intensity of the Sn–H stretching vibration in the infrared absorption spectrum. The rate increases in the order $(C_6H_5)_3SnH < (CH_3)_3SnH < (C_2H_5)_3SnH < (C_4H_9)_3SnH$. A similar sequence, $(C_6H_5)_3SnH \ll (CH_3)_3SnH < (C_2H_5)_3SnH \approx (C_4H_9)_3SnH$, was found in the hydrostannation of cyanoethyne. In conformity with these results triethyltin hydride is more reactive than trimethyltin hydride in the ionic addition to

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* At the same time these Figures demonstrate the lack of activity of the effective free radical scavenger phenoxyl; for additional data see ref. 5.

TABLE 1

SOLVENT EFFECTS FOR THE IONIC REACTION OF TRIORGANOTIN HYDRIDES WITH SUBSTITUTED ETHYNES

R_3SnH	*R'–$C{\equiv}C$–R''*			*Solvent effect*[a]
R	*R'*	*R''*	*% by volume*	k_{polar}/k_{apolar}
Me	H	COOMe	41.6	5[b]
Me	H	COOMe	29.6	9.5[b]
Et	H	COOMe	14.8	≧30[c,d]
Et	H	CN	11.7	19[c]
Me	H	CN	4.4	>150[c]
Et	H	CN	3.9	>250[e]
Me	COOEt	COOEt	2.1	7[c]
Et	COOEt	COOEt	2.1	6.5[c]
Me	CN	CN	1.7	≧90[e]
Et	CN	CN	0.8	≧80[c]

[a] The numerical values of these effects were calculated by means of the equation: $k_{polar}/k_{apolar} = t_{apolar}/t_{polar}$ in which t stands for the time required for the consumption of a given amount of hydride in the ionic reaction (see also ref. 5); polar indicates butyronitrile ($\varepsilon = 20.3$). [b] Decane ($\varepsilon = 1.99$) as apolar solvent. [c] 1,2,4-Trimethylbenzene ($\varepsilon = 2.38$) as apolar solvent. [d] o-Xylene ($\varepsilon = 2.57$) as apolar solvent. [e] Cyclohexane ($\varepsilon = 2.02$) as apolar solvent.

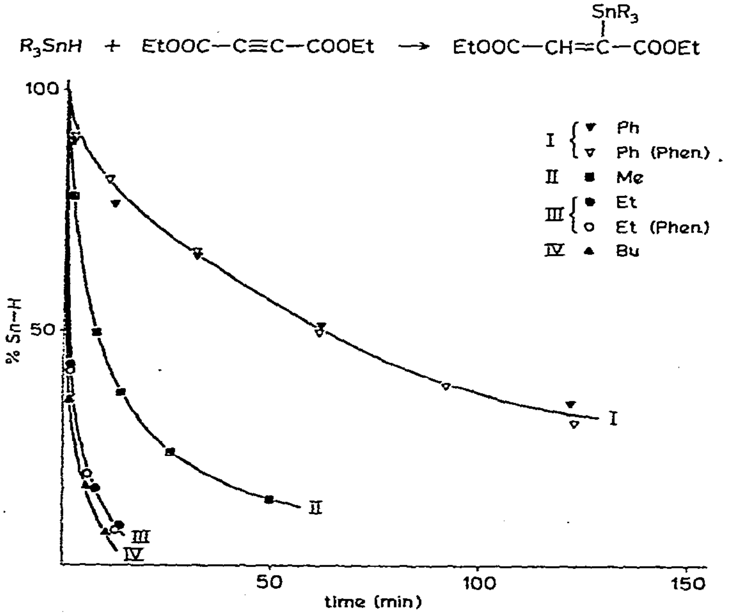


Fig. 2. Reaction of triorganotin hydrides (0.10 mole·l^{-1}) with diethyl ethynedicarboxylate (0.13 mole·l^{-1}) in butyronitrile at 21°. Phen. = 4.0 mole % (R = Ph) and 12 mole % (R = Et) of phenoxyl.

dicyanoethyne and to methyl ethynecarboxylate.

The data in Tables 2 and 3 show the effect of the substituents at the triple bond. The second order rate constants in these tables were calculated on the basis of a first order dependence on each of the reactants. First order dependence on each of the

TABLE 2

SECOND-ORDER RATE CONSTANTS FOR THE IONIC REACTION OF TRIMETHYLTIN HYDRIDE WITH SUBSTITUTED ETHYNES IN BUTYRONITRILE

R–C≡C–R'		Temp.	Second-order rate constants	
R	R'	(°C)	$k_{observed}$[a]	$k_{relative}$
H	COOMe	49.1	1.25×10^{-5}	
H	COOMe	49.4	1.05×10^{-5}	
H	COOMe	49.7	1.20×10^{-5} [b]	1[c]
H	COOMe	49.5	1.15×10^{-5} [b]	
H	CN	20.0	1.13×10^{-4}	
H	CN	20.0	1.18×10^{-4}	100
H	CN	20.4	1.28×10^{-4} [b]	
COOEt	COOEt	20.0	0.92×10^{-2}	8.000
CN	CN	20.0	$>1.5 \times 10^{-1}$	>125.000

[a] $l \cdot mole^{-1} \cdot sec^{-1}$. [b] In the presence of phenoxyl. [c] The assumption has been made that the reaction rate increases by a factor of 2–3 for each 10° rise in temperature[7].

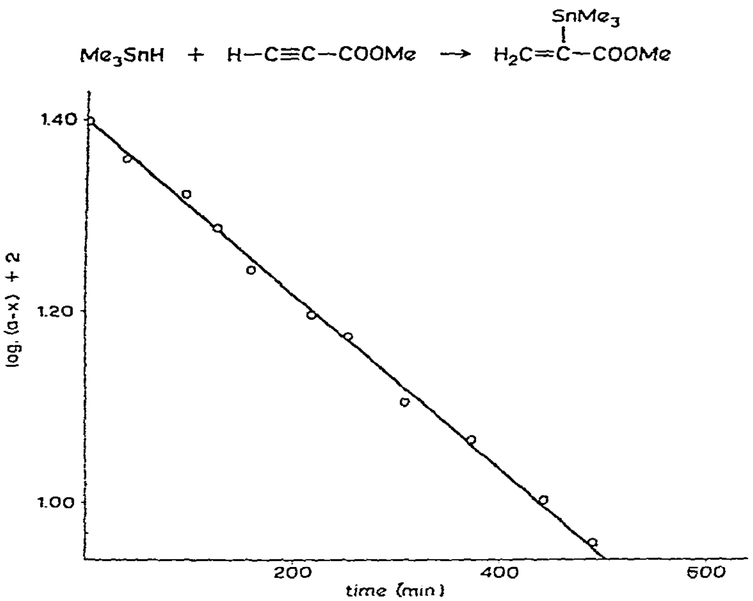
TABLE 3

SECOND-ORDER RATE CONSTANTS AND ISOTOPE EFFECTS FOR THE IONIC REACTION OF TRIETHYLTIN HYDRIDE AND DEUTERIDE WITH SUBSTITUTED ETHYNES IN BUTYRONITRILE

R–C≡C–R'		X[a]	Temp. (°C)	$k_{observed}$[b]	k_H/k_D	k_H/k_D at 20°
R	R'					
H	COOMe	H	50.3	3.80×10^{-5}		
H	COOMe	H	50.4	3.65×10^{-5}		
H	COOMe	D	50.0	3.33×10^{-5}	1.15	1.2
H	COOMe	D	50.3	3.15×10^{-5}		
H	CN	H	20.5	5.1×10^{-4}		
H	CN	D	20.5	3.6×10^{-4}	1.42	1.4
COOEt	COOEt	H	0.0			
COOEt	COOEt	H	0.0			
COOEt	COOEt	D	0.0		1.37[c]	1.3
COOEt	COOEt	D	0.0			

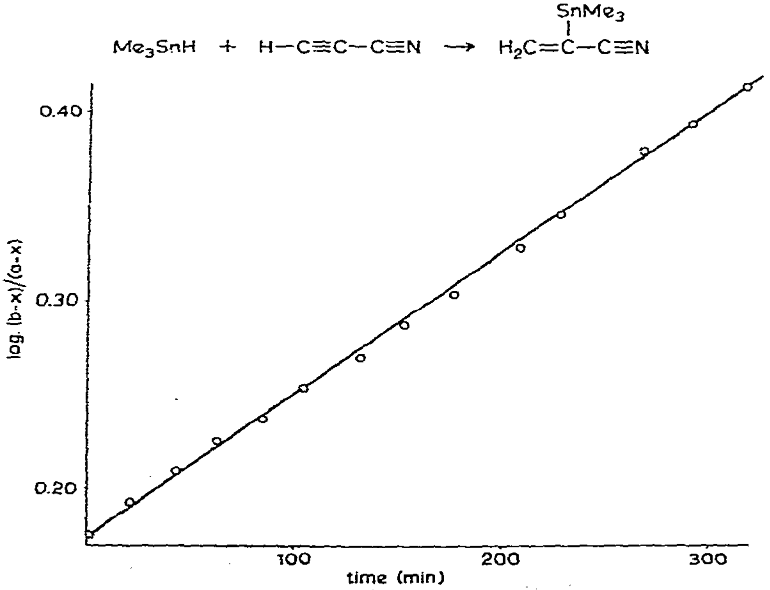
[a] X = H: triethyltin hydride; X = D: triethyltin deuteride. [b] $l \cdot mole^{-1} \cdot sec^{-1}$. [c] Calculated by means of the equations: $k_H/k_D = t_D/t_H$ in which t stands for the time required for the consumption of a given amount of hydride or deuteride (see also ref. 5).

reactants appeared from careful gas chromatographic rate measurements. The pseudo first-order plot for the ionic addition of trimethyltin hydride to methyl ethynecarboxylate, the latter compound being present in large excess, is shown in Fig. 3. In Fig. 4 the second-order plot for the reaction of trimethyltin hydride with a slight excess of cyanoethyne is shown.



$$Me_3SnH + H{-}C{\equiv}C{-}COOMe \longrightarrow H_2C{=}\overset{\overset{\displaystyle SnMe_3}{|}}{C}{-}COOMe$$

Fig. 3. Pseudo first-order plot for the ionic reaction of trimethyltin hydride (initial concentration $a = 0.252$ mole·l^{-1}) with methyl ethynecarboxylate (3.51 mole·l^{-1}) in butyronitrile at 49.4°; x = decrease in concentration of hydride in a given time t, as a result of the ionic reaction.

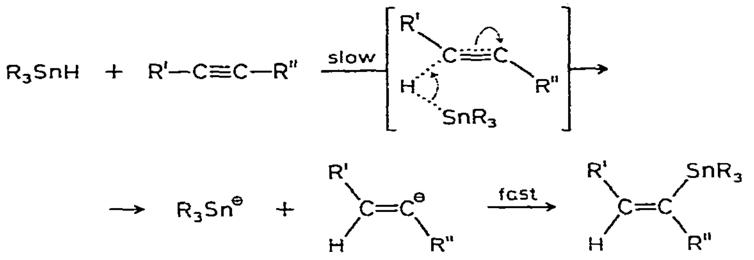


$$Me_3SnH + H{-}C{\equiv}C{-}C{\equiv}N \longrightarrow H_2C{=}\overset{\overset{\displaystyle SnMe_3}{|}}{C}{-}C{\equiv}N$$

Fig. 4. Second-order plot for the ionic reaction of trimethyltin hydride (initial concentration $a = 0.500$ mole·l^{-1}) with cyanoethyne (initial concentration $b = 0.740$ mole·l^{-1}) in butyronitrile at 20.0°; x = decrease in concentration of hydride in a given time t, as a result of the ionic reaction.

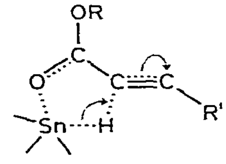
DISCUSSION

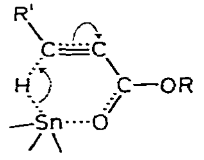
The solvent effect indicates an appreciable charge separation in the transition state of the rate determining step. From the substituent effects it can be concluded that in this transition state the tin atom has a positive and the triple bond a negative charge. Consequently, the mechanism could involve a slow hydride transfer, followed by a fast step:

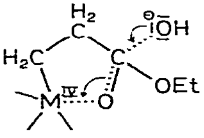


This mechanism is supported by the observed kinetics and by the isotope effect (see below).

Small solvent effects were observed in the additions to diethyl ethynedicarboxylate. In an apolar medium the reaction is comparatively fast. Apparently, in this medium the transition state is stabilized. Interaction with a second molecule of dicarboxylate does not occur since the reaction shows, in both the polar and the apolar medium, second order kinetics, first order with respect to each reactant. Probably, internal coordination of a carbonyl oxygen with the metal atom is responsible for this stabilization [(A) or (B)].


(A)


(B)


(C)

Evidently a five-membered ring (A, $R' = COOEt$) is preferred, since in additions to methyl ethynecarboxylate, in which a six-membered ring must be formed (B, $R' = H$), such an internal stabilization does not occur. These conclusions are corroborated by the observations of Rijkens and Drenth[8,9] on the rate of alkaline hydrolysis of esters of the type $Et_3M^{IV}(CH_2)_nCOOEt$ (M^{IV} = Si, Ge or Sn, $n = 2$ or 3). A stabilization of the transition state by coordination was indicated in such cases only where a five-membered ring ($n=2$) [see (C)] can arise. Six-membered rings ($n = 3$) obviously are not formed.

The reactivity sequence of R_3SnH in these additions follow the order of increasing $+I$ effect of the group R: $C_6H_5 < CH_3 < C_2H_5 \leqslant C_4H_9$. If the rate of reaction would be determined by sterical factors only, the sequence $C_6H_5 < C_4H_9 < C_2H_5 < CH_3$ had to be expected. The low reactivity of $(C_6H_5)_3SnH$ shows, that mesomeric stabilization by the phenyl groups is negligible in the transition state. As will be discussed below, it seems likely that in the transition state the hydride ion is transferred to a high degree from tin to carbon. Consequently, mesomeric stabilization is probably also negligible in the ion $(C_6H_5)_3Sn^+$.

A peculiar feature in the discussion of the deuterium isotope effect is the low stretching frequency of the Sn–H bond compared to the frequency of the C–H bond, approximately 1800 and 3000 cm^{-1}, respectively. There is a range of possibilities as to hydrogen transfer from tin to carbon in the transition state of the slow step (Fig. 5).

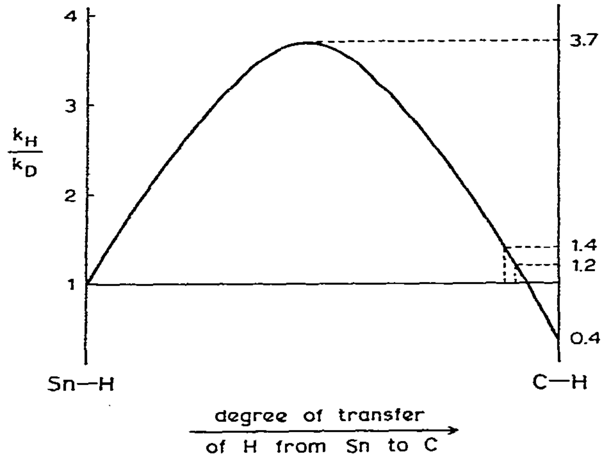


Fig. 5. Isotope effect for a hydrostannation reaction as a function of the degree of transfer of hydrogen from tin to carbon in the transition state (see text).

Three cases will be distinguished, corresponding with the left hand, the middle and the right hand regions of this figure, respectively:

(*a*) the hydrogen is still almost completely attached to tin: the isotope effect will be slightly more than unity;

(*b*) the hydrogen–tin bond is broken but the hydrogen–carbon interaction is still weak: the isotope effect will be larger than unity (theoretical value at room temperature: approximately 3.7);

(*c*) the hydrogen is completely or almost completely attached to carbon: the isotope effect will be smaller than unity as a result of the large difference between the zero-point energies of the tin–hydrogen and the carbon–hydrogen bonds.

This may be depicted schematically as in Fig. 6.

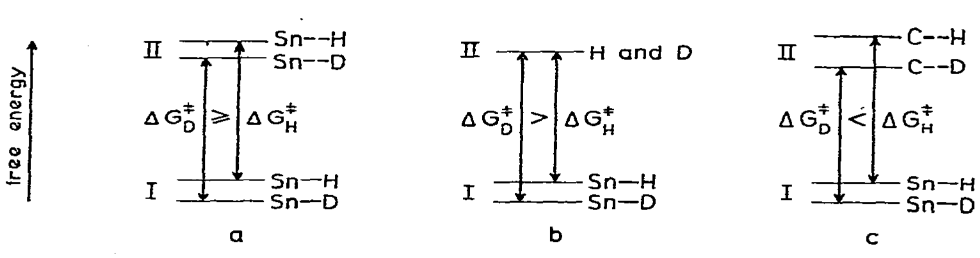


Fig. 6. Free energies of activation for the transfer of hydrogen and deuterium from tin to carbon (see text). I: initial state; II: transition state. *G* = Gibbs' free energy; in the Lewis–Randall notation called *F*.

If the hydrogen is transferred before the rate-determining step then, of course, the isotope effect will also be smaller than unity [extreme of case (*c*), theoretical value at room temperature: approximately 0.44]. In view of the fact that in all ionic additions studied the isotope effect was found to be larger than unity, it must be concluded that the hydrogen is transferred in the rate-determining step.

An extension of the Hammond postulate has led to the view that the faster a reaction proceeds the more the transition state will resemble the reactants. Thus, the transition state of the reaction of triethyltin hydride with cyanoethyne (k at 20.5° = 5.1×10^{-4} l·mole^{-1}·sec^{-1}) will be more like the reactants than the transition state of the reaction of triethyltin hydride with methyl ethynecarboxylate (k at 50.3° = 3.7×10^{-5} l·mole^{-1}·sec^{-1}). Since in these reactions the isotope effects (at 20°) are 1.4 and 1.2 respectively, it must be concluded that in the transition state the hydrogen is transferred to a high degree from tin to carbon* (see also Fig. 5). This implies that the transition state has a considerable ionic character, which is in accord with the substantial solvent effects as well as with the observation that the response to the presence of electron-withdrawing groups at the triple bond is large. The isotope effect for the reaction of triethyltin hydride with diethyl ethynedicarboxylate does not fit completely into this picture. The observed value of 1.3 is smaller than the value expected for this fast reaction (>1.4). Probably the discrepancy is the result of internal solvation which, as has been discussed before[5], also may be partly operative in the solvent used in these experiments (butyronitrile).

In conclusion, it appears that hydrostannation of electrophilic ethynes proceeds by an ionic mechanism in which nucleophilic attack of the hydride hydrogen on carbon is the first and rate-determining step. Thereupon the organotin cation generated in this step adds *trans* to the vinyl carbanion. In the transition state of the slow step the hydride hydrogen is transferred to a high degree from tin to carbon.

In the hydrostannation of diethyl ethynedicarboxylate most probably a five-membered cyclic transition state is involved.

EXPERIMENTAL PART

All reactions and subsequent manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen. Liquids were handled by the syringe technique. Starting materials were purchased or prepared according to published procedures. Solvents were carefully purified and dried by conventional methods. All liquid materials were distilled before use in an atmosphere of nitrogen either at normal or at reduced pressure.

Gas chromatographic analyses were made by means of F & M Gas Chromatographs Models 500 and 810 with katharometer detection, using helium as a carrier gas. In these analyses, which were performed by Miss G. G. de Haan and Miss E. Ch. Th. Gevers, the following columns have been used:

Column 1: 12′ stainless steel column 1/4″ OD, packed with 20% Silicone Oil DC 710 on Diatoport WAW 60–80 mesh;

Column 2: 4′ stainless steel column 1/4″ OD, packed with 10% Silicone Gum Rubber SE 30 on Diatoport S 60–80 mesh;

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* On similar considerations as discussed above Dessy[10] concluded that in the acetolysis of tributyltin hydride bonding between the two participating hydrogens is almost complete in the transition state.

Column 3: 12′ stainless steel column 1/4″ OD, packed with 15% Carbowax 20 M on Diatoport S 60–80 mesh.

NMR spectra, which were run by Mr. M. J. A. de Bie (Laboratory of Organic Chemistry, State University of Utrecht) and Miss L. Veldstra, were recorded using a Varian Associates A-60 NMR spectrometer* and a Varian Associates HR-100A NMR spectrometer.

IR spectra, which were run by Miss G. E. E. Woldringh, Miss L. Veldstra and Miss H. Alberda, were recorded using a Perkin–Elmer spectrophotometer type Infracord 137 and a Grubb Parsons Spectromaster.

As examples of the procedures followed two experiments will be described in detail.

Addition of trimethyltin hydride to cyanoethyne as followed by means of gas chromatography

Cyanoethyne (3.70 mmoles) was dissolved in a mixture of 4.06 ml of butyronitrile and 0.37 ml of 1,2,4-trimethylbenzene (internal standard). The reaction flask was placed in a thermostat, kept at 20.0° and 2.50 mmoles of trimethyltin hydride were added at once. At appropriate time intervals 5 μl samples were taken from the reaction mixture and analyzed by means of gas chromatography [F & M Gas Chromatograph Model 500; column 3; temperature of injection port: 190°; column temperature: 125° isothermal; block temperature: 240°; bridge current: 150 mA; carrier gas (helium) velocity: 69 ml/min].

The peak areas due to reactants and products were corrected for inaccuracies in the amount of sample and for instrumental deviations by means of the internal standard. When plotting the corrected peak areas due to products against the corrected peak areas due to the hydride and against the corrected peak areas due to the ethyne straight lines were obtained (by least-squares treatments). From these relations the ratios of the responses of products and reactants, and the peak areas of the reactants at the start of the reaction were determined. Similarly, a straight line was obtained by plotting the areas due to the hydride against the areas due to the ethyne, indicating that these compounds react exactly in a 1:1 ratio. From the intercept of this straight line the excess of ethyne was calculated, the magnitude of which was in accord with the excess calculated from the amounts brought together at the start of the reaction. In this way the individual responses of the components were determined, the correctness of this procedure being confirmed by calibration with the pure components.

In the calculation of the second-order rate constant of the ionic reaction the simultaneous formation of the *cis*-β-adduct, originating from the free radical reaction, had to be taken into account. Fortunately, under the conditions employed only small amounts of the β-adduct were formed in a fast reaction that stopped almost completely within 2 minutes. Thus, only a small correction had to be made, after which the second-order rate constant was calculated.

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* The authors are much indebted to Professor J. F. Arens (Laboratory of Organic Chemistry, State University of Utrecht) for making available the 60 MHz NMR spectrometer.

Addition of triethyltin hydride to cyanoethyne as followed by means of infrared spectroscopy

In a small reaction flask, kept at 20.0°, were introduced successively 2.28 ml of solvent (see below), 0.119 ml (0.72 mmole) of triethyltin hydride and 0.097 ml (1.50 mmoles) of cyanoethyne (initial concentrations: 0.29 mole·l^{-1} triethyltin hydride and 0.60 mole·l^{-1} cyanoethyne). At appropriate time intervals samples (about 0.05 ml) were drawn from the solution. The rate of reaction was derived from the intensity of the Sn–H absorption band at about 1800 cm^{-1} in the IR spectra of these samples. The intensity of the Sn–H band at $t = 0$ min was calculated from the IR spectrum run before the addition of the ethyne, taking into account its volume. During the reaction the intensity of the C≡N absorption band at about 2200 cm^{-1} of the product increased linearly with the decrease of the intensity of the Sn–H absorption band.

In this way the rate of reaction was determined in: cyclohexane, ethanol, butyronitrile, butyronitrile in the presence of 2.8 mole % of phenoxyl, methanol, acetonitrile and N,N-dimethylacetamide. The relative rate constants in these solvents were found to be: < 0.004 (cyclohexane), 0.65 (ethanol), 1.0 (butyronitrile, both in the absence and in the presence of phenoxyl), 1.9 (methanol and acetonitrile) and 5.5 (N,N-dimethylacetamide).

The experiment in ethanol was repeated using trimethyltin hydride instead of triethyltin hydride. The NMR spectrum, run at the end of the experiment (conversion: 90%), revealed that exclusively the α-adduct had been formed in quantitative yield.

ACKNOWLEDGEMENT

The authors are much indebted to Professor G. J. M. VAN DER KERK for his stimulating interest and to Dr. J. G. NOLTES and Mr. J. W. MARSMAN for helpful discussions. Part of this work was sponsored by the International Tin Research Council. The authors are indebted to Dr. E. S. HEDGES for permission to publish.

SUMMARY

Mechanistic aspects of the hydrostannation of electrophilic ethynes have been studied. As appears from stereochemical data, kinetics, and substituent, solvent and isotope effects, the addition reaction proceeds by a *trans*-mechanism in which nucleophilic attack of the hydride hydrogen on carbon is the first and rate-determining step.

In the hydrostannation of diethyl ethynedicarboxylate most probably a five-membered cyclic transition state is involved.

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