Tetrahedron Letters No.3, pp. 335-340, 1966. Pergamon Press Ltd.
Printed in Great Britain.

MECHANISM OF THE HYDROSTANNATION OF ACRYLONITRILE

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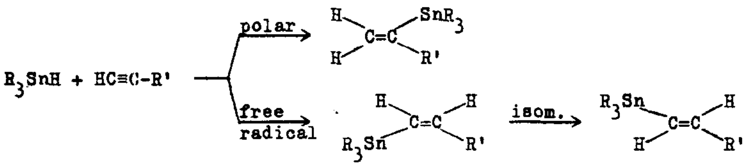
(Received 22 November 1965)

During the past decade the addition of organotin hydrides across a variety of unsaturated bonds has been described(1-3). The greater part of these hydrostannation reactions proceeds in the absence of catalysts under mild conditions(4-7). Free radical-generating species(8-10) and U.V.-irradiation(11, 12) accelerate the hydrostannation of olefinic, acetylenic and carbonyl compounds. Recently zinc chloride has been reported(9, 10) to accelerate the hydrostannation of carbonyl derivatives and azomethines.

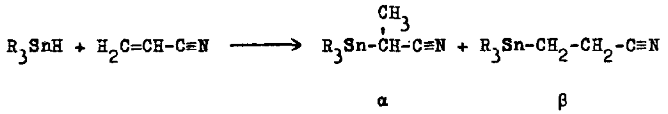
Although the mechanistic aspects of these additions had not been studied in detail, the hydrostannation reaction generally has been regarded to proceed *via* a free radical mechanism(2, 3). Whereas this would be expected to hold true under free radical-generating conditions (AIBN, UV-light), we have shown(13, 14) quite recently that the hydrostannation of the C=N bond of isocyanates and of the C=S bond of isothiocyanates proceeds *via* a polar mechanism, even in the presence of AIBN.

From their mechanistic studies concerning the addition of triethyltin hydride to some terminal and non-terminal olefins and to phenylacetylene, Neumann and Sommer(15) concluded that in the non-catalyzed hydrostannation of carbon-carbon double and triple bonds a free radical mechanism is operative. However, we recently presented(16) convincing evidence that the addition of trialkyltin hydrides to carbon-carbon triple bonds can proceed via a polar mechanism (leading to the α-adducts) as well as via a free radical mechanism (leading to the β-adducts):



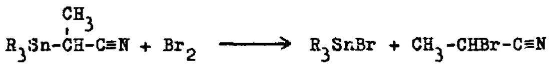
These results induced us to study the nature of the hydrostannation reaction of olefinic compounds more closely. The present paper reports on the addition of tri-organotin hydrides to acrylonitrile.

The organotin hydrides were reacted with acrylonitrile at 50-75° under nitrogen in an 1:1, 2:3 and 1:2 ratio. As appeared from gas chromatography in the greater part of the experiments two compounds are formed, which have been identified by means of NMR spectroscopy and elementary analysis as the α- and β-adducts:



$$R_3SnH + H_2C{=}CH{-}C{\equiv}N \longrightarrow \underset{\alpha}{R_3Sn{-}\overset{CH_3}{CH}{-}C{\equiv}N} + \underset{\beta}{R_3Sn{-}CH_2{-}CH_2{-}C{\equiv}N}$$

Degradation of the α-adduct with bromine yielded α-bromo-propionitrile, which is in accordance with the assigned structure(17):



$$R_3Sn{-}\overset{CH_3}{CH}{-}C{\equiv}N + Br_2 \longrightarrow R_3SnBr + CH_3{-}CHBr{-}C{\equiv}N$$

Until now the presence of α-adducts in the hydrostannation products of olefins had not been observed.

In Table I the results of some experiments are summarized. In the experiments involving trialkyltin hydrides the α-adduct is always formed in the absence of the free radical initiator AIBN. Obviously the latter only catalyzes the formation of the β-adduct (Run nos. 7 and 10).

TABLE I

Hydrostannation of Acrylonitrile

Run no.	Substit. on Tin	Ratio SnH:olefine	Reaction temp., °C	Reaction time, hrs.	Conversion %	Ratio α:β
1	Me	1:1	50	41	> 80	25:75
2	"	1:1	50	46	> 90	15:85
3	"	2:3	50	23	~ 80	15:85
4	"	2:3	50	40	> 70	25:75[a]
5	"	2:3	50	46	~ 90	15:85[a]
6	Et	2:3	75	4	~100	80:20
7	"	2:3	75	$1^1/_2$	~100	0:100[b]
8	"	2:3	75	3	> 90	80:20[a]
9	"	2:3	75	7	~100	70:30[a]
10	"	2:3	75	$^1/_2$	~100	0:100[a,b]
11	"	1:2	60	14	~100	70:30[a]
12	*i*-Pr	2:3	75	24	> 90	15:85
13	*n*-Bu	2:3	75	8	> 90	30:70
14	"	2:3	75	16	~100	60:40[a]
15	Ph	2:3	60	3	~100	0:100[a]

[a] With non-stabilized acrylonitrile

[b] In the presence of 2 mole % of AIBN

Experiments in polar and non-polar solvents, in which the rate of formation of the adducts has been followed by means of GLC, reveal a negligible solvent effect for the formation of the β-adduct, whereas the rate of formation of the α-adduct increases with increasing polarity of the solvent. Addition of AIBN enhances considerably the rate of formation of the β-adduct, but not that of the α-adduct. The solvent effect makes a four-centre type transition state(18) in the formation of the α-adduct less probable. In conclusion, it appears that in the formation of the α-adduct a polar mechanism is operative, whereas the β-adduct is formed via a free radical mechanism.

The rate of the polar reaction has been found to increase in the sequence $Ph_3SnH < Me_3SnH \approx$ i-$Pr_3SnH <$ n-$Bu_3SnH < Et_3SnH$. When the rate of reaction is determined by sterical factors only, the sequence $Ph_3SnH <$ i-$Pr_3SnH <$ n-$Bu_3SnH < Et_3SnH < Me_3SnH$ has to be expected. In view of the low reactivity of trimethyltin hydride also inductive effects must play a part in the polar addition. Obviously, the rate of reaction is decreased by bulky substituents and increased by electron-releasing substituents on tin. Hydrostannation of methyl acrylate under the same conditions yielded exclusively the β-adduct. This implies that the polar reaction is retarded if the cyano group is replaced by less electron-withdrawing groups. These facts are in accordance with a nucleophilic attack of the organotin hydride hydrogen on carbon as the rate-determining step in the polar reaction. Similar results have been obtained in the hydrostannation of electrophilic acetylenes(16) ($Ph_3SnH \ll Me_3SnH < Et_3SnH \approx Bu_3SnH$), in which sterical effects are expected to be less important than in additions to ethylenes(19).

Contrary to the above described results Neumann and Sommer(15) concluded that the addition of triethyltin hydride to acrylonitrile proceeds exclusively via a free radical mechanism. However, they only demonstrated the catalytic activity of free radical sources, which proves that the reaction can proceed via a free radical mechanism.

It should be noted that, in view of the lower electrophilic character of the carbon-carbon double bond as compared with the corresponding triple bond and the greater reactivity of the first in free radical reactions, hydrostannation of weakly electrophilic and nucleophilic carbon-carbon double bonds preferentially will proceed *via* a free radical mechanism.

These studies concerning the mechanistic aspects of hydrostannation reactions are being continued.

Acknowledgement. The authors wish to thank Professor G.J.M.van der Kerk for his stimulating interest, Dr.W.Drenth and Mr.J.W.Marsman for discussions and Mr.H.A.Budding for able experimental assistance.

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