

STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXIV*. STRUCTURE OF PRODUCTS OBTAINED IN THE HYDROSTANNATION OF ETHYNES**

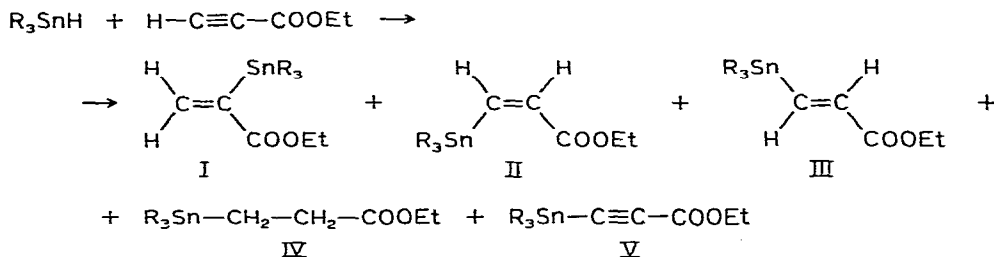
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INTRODUCTION

In a previous paper² we have shown that in reactions of trialkyltin hydrides with alkyl ethynecarboxylates in the absence of solvents and catalysts a variety of compounds are formed, *e.g.*:



(Ia–Va, R = Me; Ib–Vb, R = Et)

Similar reactions of trialkyltin hydrides with propynol, ethyl 1-propyne-carboxylate, cyanoethyne and diethyl ethynedicarboxylate led only to the formation of the unsaturated 1:1 adducts³.

In the present paper the results of a further study of these reactions are presented.

RESULTS

Organotin monohydrides were brought into reaction with a variety of mono- and disubstituted ethynes. The identity of the resulting products was established by means of elementary analysis, infrared absorption spectroscopy and proton magnetic resonance spectroscopy. The yields of the several products were calculated from NMR spectra and gas chromatograms of the reaction mixtures.

NMR data of the compounds identified in this and previous studies are presented in Tables 1–3. In previous papers^{2,3} structural assignments were based mainly upon the coupling constants, $J(H-H)$, of the olefinic protons and on the

* Part XXIII: see ref. 1.

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

TABLE I. NMR DATA OF COMPOUNDS (I)-(X)

Compounds	Chemical shifts ^a (ppm ^b) and coupling constants (Hz)						
	H _a	H _b	H _c	J _{ab}	J _{cd}	J(Sn-H _a) ^c	J(Sn-H _b) ^c
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Me (Ia)	d 6.86	d 5.91	q 4.15	2.8	7.2	123.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (Ib)	d 6.88	d 5.90	q 4.16	3.0	7.1	128.0 118.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Me (IIa)	d 7.10	d 6.66	q 4.18	12.6	7.2	66.5
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (IIb)	d 7.10	d 6.71	q 4.21	12.6	7.1	70.0 64.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Me (IIIa)	d 7.65	d 6.26		19.5		
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (IIIb)	d 7.60	d 6.24	q 4.15	19.5	7.2	61.0 54.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Me (IVa)	t 0.94	t 2.50		7.5		50.5
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (IVb)		t 2.48	q 4.18		7.1	66.5
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (Vb)			q 4.13		7.1	
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Me (VIa)	d 6.83	d 5.93	s 3.71	3.0		122.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (VIb)	d 6.85	d 5.90	s 3.68	2.9		127.5 115.5
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Pr (VIc)	d 6.83	d 5.90	s 3.69	3.0		110.5 114.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Me (VIIa)	d 7.11	d 6.66	s 3.69	12.7		108.5
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (VIIb)	d 7.12	d 6.72	s 3.70	12.6		65.5
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Pr (VIIc)	d 7.12	d 6.67	s 3.68	12.7		68.0 63.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Me (VIIIa)	d 7.65	d 6.23		19.3		62.0 122.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (VIIIb)	d 7.63	d 6.26	s 3.73	19.5	~61	65.0 ~55
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Pr (VIIIc)	d 7.63	d 6.25	s 3.73	19.5	61.0	62.0 54.0
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Me (IXa)	t 0.98	t 2.50	s 3.61	7.5	~50.0	65.0 ~66.5
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (IXb)	t 0.97	t 2.49	s 3.60	7.7		~57
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Pr (IXc)		t 2.47		7.7		
$\begin{array}{c} \text{H}^a \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H}^b \quad \text{COOCH}_2\text{CH}_3^d \end{array}$	R = Et (Xb)			s 3.67			

^a Only multiplicities due to H-H coupling are given; s: singlet; d: doublet; t: triplet; q: quartet. ^b Downfield from tetramethylsilane, internal. ^c Coupling constants with ¹¹⁷Sn and ¹¹⁹Sn isotopes, respectively.

TABLE 2. NMR DATA OF COMPOUNDS (XI)-(XXI)

Compounds	Chemical shifts ^a (ppm ^b) and coupling constants (Hz)						
	H _a	H _b	J _{ab}	J _{ac}	J _{bc}	J(Sn-H _a) ^c	J(Sn-H _b) ^c
	d 5.86 t	d 5.18 t	2.5	<1.0	<1.0		
(XIb)	d 5.92 t	d 5.37 t	2.0	<1.0	<1.0		
(XIIa)	d 5.94 t	d 6.65 t	12.5	<1.0	5.0	~68	~135
(XIIb)	d 6.25 t	d 6.74 t	12.9	<1.0	3.2		
(XIIIa)	b 6.12 b 6.3	b 6.12 b 6.3					~70
(XIVa)	q 7.39 q 7.41	d 1.90 d 1.86	7.0			118.0 108.0	123.0 112.5
(XVb)	d 2.05 d 2.00	q 6.24 q 6.18	6.9 7.0				61.5 64.5
(XVIa)	d 2.13 d 2.11	q 6.34 q 6.36	1.7 1.6				~116 ~109
(XVIIa)	d 6.63 d 6.65	d 6.10 d 6.06	2.6 2.6			97.5 88.0	102.0 92.0
(XVIIc)	d 6.62 d 6.62	d 6.04 d 6.04	2.7			88.5	92.5 44.5 46.5
(XVIIIa)	d 7.29	d 6.18	14.7			54.0	56.0 106.5 111.5

(continued overleaf)

^a Only multiplicities due to H-H coupling are given; s: singlet; d: doublet; t: triplet; q: quartet; b: unresolved broad signal. ^b Downfield from tetramethylsilane internal. ^c Coupling constants with ¹¹⁷Sn and ¹¹⁹Sn isotopes, respectively.

TABLE 2 (continued)

Compounds	Chemical shifts ^a (ppm ^b) and coupling constants (Hz)					
	H _a	H _b	J _{ab}	J _{ac}	J _{bc}	J(Sn-H _b) ^c
	d 7.54	d 5.75	20.4			
(XIXa) R = Me						
	s 6.81					92.5
(XXa) R = Me						97.0
(XXb) R = Et	s 6.83					83.5
(XXc) R = Bu	s 6.77					87.5
(XXd) R = Ph	s 7.05					83.0
						87.0
						112.5
						117.0
	s 5.97					58.0
(XXIa) R = Me						60.5
(XXIb) R = Et	s 5.94					50.0
(XXIc) R = Bu	s 5.92					49.5
						52.0

^a Only multiplicities due to H-H coupling are given; s: singlet; d: doublet; t: triplet; q: quartet; b: unresolved broad signal. ^b Downfield from tetramethylsilane internal. ^c Coupling constants with ¹¹⁷Sn and ¹¹⁹Sn isotopes, respectively.

TABLE 3. NMR DATA OF COMPOUNDS (XXII)-(XXXIV)

Compounds	Chemical shifts ^a (ppm ^b) and coupling constants (Hz)					
	H _a	H _b	J _{ab}	J _{ac}	J _{bc}	J(Sn-H _b) ^c
	s 6.44 (in cyclohexane)					66.5
(XXIIa) R = Me						69.5
	s 6.75 (in butyronitrile)					60.5
(XXIIb) R = Et						63.0
	s 6.47 (in cyclohexane)					59.0
	s 6.83 (in butyronitrile)					61.0
						56.0
	d 5.76	d 6.42	12.5	1.0	7.2	~82
(XXIVa) R = Me						~154
	d 5.70	d 6.49	12.5	1.7	7.0	~73
(XXIVb) R = Et						~143
	d 6.11	d 6.75	12.0	0.8	6.8	~92?
(XXIVc) R = Ph						~176?

$\begin{array}{c} \text{R}_3\text{Sn} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{CH}_2-\text{C}_3\text{H}_7 \end{array}$	(XXVa) R = Me (XXVb) R = Et (XXVc) R = Ph	b 5.92 b 5.88 b 6.25	b 5.92 b 5.88 b 6.25	~84 ~73 ~90?
$\begin{array}{c} \text{R}_3\text{Sn} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{Ph} \end{array}$	(XXVIIa) R = Me (XXVIIb) R = Et (XXVIIc) R = Ph	d 7.55 d 7.62 d 7.80	d 6.15 d 6.15 d 6.43	~66? 57.0 ~70
$\begin{array}{c} \text{R}_3\text{Sn} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{Ph} \end{array}$	(XXVIIIa) R = Me (XXVIIIb) R = Et	b 6.82 b 6.83	b 6.82 b 6.83	~148? 132.5 ~164
$\begin{array}{c} \text{R}_3\text{Sn} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{OEt} \end{array}$	(XXIXa) R = Et	d 4.00	d 4.64	~64
$\begin{array}{c} \text{R}_3\text{Sn} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{OEt} \end{array}$	(XXXa) R = Et (XXXb) R = Ph	d 6.73 d 6.82	d 4.46 d 4.88	46.5 58.0
$\begin{array}{c} \text{R}_3\text{Sn} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{OEt} \end{array}$	(XXXIa) R = Et (XXXIb) R = Ph	d 6.19 d 6.46	d 4.46 d 4.89	97.0 121.0
$\begin{array}{c} \text{R}_3\text{Sn} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{SBu} \end{array}$	(XXXIIIa) R = Et	d 7.07	d 6.00	122.0
$\begin{array}{c} \text{R}_3\text{Sn} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{SBu} \end{array}$	(XXXIVa) R = Et	d 6.42	d 5.91	62.5
		18.5	11.4	59.5
				127.5
				61.0

^a Only multiplicities due to H-H coupling are given; s: singlet; d: doublet; t: triplet; b: unresolved broad signal. ^b Downfield from tetramethylsilane internal.

^c Coupling constants with ¹¹⁷Sn and ¹¹⁹Sn isotopes, respectively.

differences between the chemical shifts, $\Sigma\Delta\delta_{ct}$, of *cis*- and *trans*-olefinic protons as a result of differential shielding by β -substituents (see also ref. 3). These assignments have now been confirmed by the magnitude of the observed coupling constants of the olefinic protons with ^{117}Sn and ^{119}Sn isotopes. In general it appears that:

- (a) $|J(\text{Sn}-\text{H}_{gem})|$ is slightly larger than $|J(\text{Sn}-\text{H}_{cis})|$, while $|J(\text{Sn}-\text{H}_{trans})|$ is about two times as large as $|J(\text{Sn}-\text{H}_{cis})|$;
 (b) the absolute values of these coupling constants are lowered by electron-withdrawing substituents at the double bond.

In Table 4 a survey is given of the results obtained in the hydrostannation of monosubstituted ethynes. As appears from this Table hydrostannation of these ethynes afforded both α - and β -adducts:

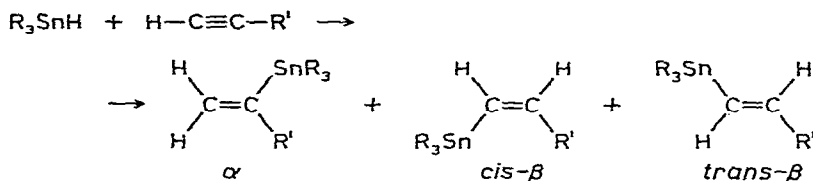


TABLE 4

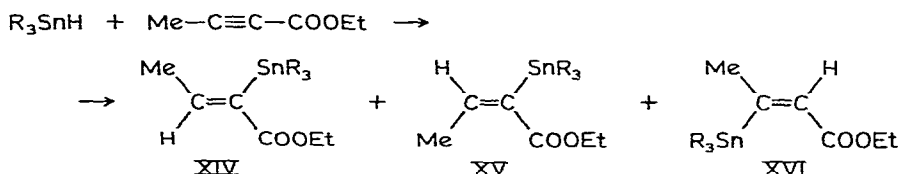
HYDROSTANNATION OF MONOSUBSTITUTED ETHYNES

Exp. No.	R	R'	Reaction conditions	1:1 adducts	
				Total yield	Structures and ratio α /cis- β /trans- β
1 ^a	Me	COOEt	$\begin{cases} 18 \text{ h, } 55^\circ \\ 4 \text{ h, } 80^\circ \end{cases}$	41%	(Ia)/(IIa)/(IIIa) = 67:25:8
2 ^a	Me	COOMe	23 h, 55°	40%	(VIa)/(VIIa)/(VIIIa) = 81:15:4
3 ^a	Et	COOMe	23 h, 55°	57%	(VIb)/(VIIb)/(VIIIb) = 58:24:18
4 ^a	Pr	COOMe	5½ h, 55°	72%	(VIc)/(VIIc)/(VIIIc) = 31:36:33
5	Et	CH ₂ OH	6 h, 100°	>70%	(XIa)/(XIIa)/(XIIIa) = 25:45:30
6	Ph	CH ₂ OH	$\begin{cases} 3 \text{ h, } 60^\circ \\ 16 \text{ h, } 20^\circ \end{cases}$	80%	(XIb)/(XIIb)/(XIIIb) = 5:45:50
7	Me	CN	1 h, 20°	100%	(XVIIa)/(XVIIIa)/(XIXa) = 100:0:0
8	Et	CN	1 h, 20°	100%	(XVIIb)/(XVIIIb)/(XIXb) = 100:0:0
9	Pr	CN	1 h, 20°	100%	(XVIIc)/(XVIIIc)/(XIXc) = 100:0:0
10	Me	Bu	7 h, 60°	85%	(XXIIIa)/(XXIVa)/(XXVa) = 2:29:69
11	Et	Bu	6 h, 50°	55%	(XXIIIb)/(XXIVb)/(XXVb) = 3:51:46
			$\begin{cases} 12 \text{ h, } 50^\circ \\ 16 \text{ h, } 20^\circ \end{cases}$	85%	= 3:31:66
12	Ph	Bu	3 h, 50°	>80%	(XXIIIc)/(XXIVc)/(XXVc) = 0:85:15
13	Me	Ph	66 h, 50°	75%	(XXVIa)/(XXVIIa)/(XXVIIIa) = 6:66:28
14	Et	Ph	7 h, 60°	75%	(XXVIb)/(XXVIIb)/(XXVIIIb) = 0:70:30
15	Ph	Ph	$\begin{cases} 2 \text{ h, } 20^\circ \\ 1 \text{ h, } 60^\circ \end{cases}$	90%	(XXVIc)/(XXVIIc)/(XXVIIIc) = 0:28:72
16	Et	OEt	1½ h, 50°	100%	(XXIXa)/(XXXa)/(XXXIa) = 4:91:5
17	Ph	OEt	1 h, 20°	>90%	(XXIXb)/(XXXb)/(XXXIb) = 0:97:3
18 ^b	Et	SBu	3 h, 45°	70%	(XXXIIa)/(XXXIIIa)/(XXXIVa) = 0:77:23

^a In these experiments also other products are formed, viz. (IV), (V), (IX), (X) and 2:1 adducts (see also Table 1 and ref. 2). ^b In the presence of butyronitrile.

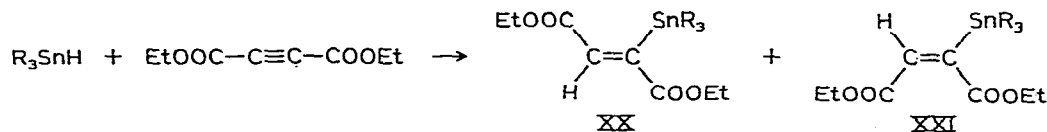
For a discussion of the structural assignments the reader is referred to previous papers²⁻⁴. Experiments 1-5 and 7-9 have been described before. In the latter experiments exclusively the α -adduct is formed. Detectable amounts of the *cis*- and *trans*- β -adducts (XVIII) and (XIX) are formed under special conditions only⁴, viz. in the presence of both an apolar solvent (retardation of the rate of formation of the α -adduct) and a free radical initiator (acceleration of the rate of formation of the β -adducts). The gas chromatograms of the reaction mixtures obtained in experiments 10, 11 and 13 displayed three peaks, which obviously arise from 1 : 1 adducts. As appeared from NMR data the two main peaks are due to the *cis*- β - and *trans*- β -adducts. The small third peak was assigned to the α -adduct. The correctness of this assignment could not be verified by NMR spectroscopy as a result of the low concentration of this isomer in the NMR samples. In experiment 14 only two peaks arising from 1 : 1 adducts (*cis*- and *trans*- β -adduct) were observed in the gas chromatogram. However, this does not exclude the presence of a very small amount of the α -adduct, which might have escaped detection by NMR spectroscopy as well. Similarly, in the NMR spectra of the reaction mixtures from triphenyltin hydride and 1-hexyne (exp. 12) and ethoxyethyne (exp. 17) and from triethyltin hydride and butylthioethyne (exp. 18) only signals due to the β -adducts could be detected, but also in these cases very small amounts of the α -adducts may be present. In the NMR spectrum of the reaction mixture from triphenyltin hydride and phenylethyne (exp. 15) the olefinic protons of the *trans*- β -adduct are obscured by the phenyl signal. Since approximately 90% of the ethyne had reacted yielding 25% of the *cis*- β -adduct (XXVIIc), it was concluded that about 65% of the *trans*- β -adduct (XXVIIc) had been formed. A pure sample of the latter adduct was isolated from the reaction mixture.

As has been reported before³ at last three 1 : 1 adducts were formed in the hydrostannation of ethyl 1-propynecarboxylate. Two of these adducts appeared to be the isomeric α -adducts (XIV) and (XV). In view of the fact that mainly *trans*-addition occurred in this type of additions structure (XVI) was tentatively assigned to the third adduct.



(XIVa)-(XVIa), R = Me; (XIVb)-(XVIb), R = Bu; (XIVa)/(XVa)/(XVIa) = 59 : 9 : 32
(XIVb)/(XVb)/(XVIb) = 50 : 13 : 37

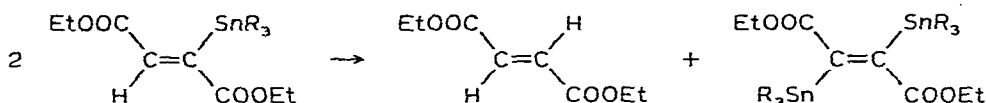
The correctness of this assignment has now been proven by the *trans*-coupling of the olefinic proton of (XVI) with ¹¹⁷Sn and ¹¹⁹Sn isotopes. Similarly, the assignment of structures (XX) and (XXI) [(XX)/(XXI) \approx 9 : 1] to the adducts formed in quantitative



(XXa)-(XXIa), R = Me; (XXb)-(XXIb), R = Et; (XXc)-(XXIc), R = Bu

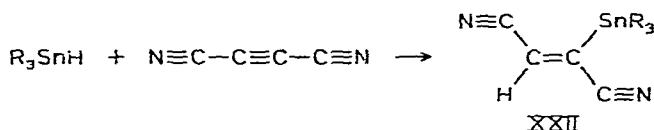
yield in the reaction of trialkyltin hydrides with diethyl ethynedicarboxylate has now been proven by the $^{117,119}\text{Sn}-\text{H}_{\text{olef}}$ coupling constants of both (XX) and (XXI).

Incidentally, very small amounts of diethyl fumarate were found to be present in the reaction mixtures. Most probably diethyl fumarate is formed by disproportionation of the primary adducts*, *e.g.*:



Addition of triphenyltin hydride to the diethyl ethynedicarboxylate at 20° in the presence of solvents (cyclohexane or butyronitrile) afforded mixtures in which adduct (XXd) and diethyl fumarate were present in a ratio of approximately 5:1. The yield calculated on the amount of hydride consumed (85% in butyronitrile and 70% in cyclohexane) was quantitative, assuming that diethyl fumarate is formed by disproportionation of the 1:1 adduct.

Hydrostannation of dicyanoethyne in the presence of the same solvents as above afforded one adduct (singlet in the olefinic region) in more than 80% yield.



(XXIIa), R = Me; (XXIIb), R = Et

The assignment of structure (XXII) to this adduct is based on the magnitude of the coupling constants of the olefinic proton with the ^{117}Sn and ^{119}Sn isotopes (~ 60 Hz).

As mentioned above the absolute values of the $^{117,119}\text{Sn}-\text{H}_{\text{olef}}$ coupling constants are lowered by the presence of electron-withdrawing groups at the double bond. Since J_{trans} and J_{cis} in a compound like (XVIIIb) with one cyano group attached to the double bond, have been found to be 90 and 45 Hz, it must be expected that in compound (XXIIb) and its isomer J_{trans} and J_{cis} are much lower than 90 and 45 Hz, respectively. Consequently, it must be concluded that compound (XXII) is the main product in this type of reaction. The presence of its isomer could not be detected. Furthermore, the NMR spectra revealed the presence of very small amounts of 1,2-dicyanoethene, which might have been formed by disproportionation of the 1:1 adduct (see above).

CONCLUSIONS

The experiments described above demonstrate that in reactions of organotin monohydrides with ethynes in general a mixture of products is formed. Apart from

* Similar disproportionations have been observed with adducts from triethyltin hydride and diethyl azodicarboxylate⁵ and from triphenylplumbyllithium and diethyl ethynedicarboxylate⁶, while attempts to distill the adduct from trimethyllead hydride and diethyl ethynedicarboxylate (diethyl trimethylplumbyl-fumarate) resulted in the formation of diethyl fumarate and unidentified materials⁷.

the formation of 2 : 1 adducts and of some other products in the case of ethynemonocarboxylates it appears that:

- (a) addition of trialkyltin hydrides to monosubstituted ethynes containing a strongly electron-withdrawing substituent (COOR , $\text{C}\equiv\text{N}$) affords mainly, or even exclusively, the α -adduct;
- (b) addition of organotin monohydrides to monosubstituted ethynes containing an electron-releasing (C_4H_9 , OC_2H_5) or a weakly electron-withdrawing (CH_2OH , C_6H_5) substituent affords mainly the *cis*- and *trans*- β -adducts, in addition to small amounts of the α -adduct;
- (c) addition of trialkyltin hydrides to disubstituted ethynes affords mainly the *trans*-addition products.

As may be derived from the experiments involving ethyl 1-propynecarboxylate and 1-hexyne the *cis*- α - as well as the *cis*- β -adduct seems to be the primary adduct (occurrence of *trans*-addition), which is in accord with similar observations in the case of phenylethyne⁸.

Non-terminal addition (formation of α -adducts) although of minor importance in some of these hydrostannations, has been observed in almost all cases studied. Consequently, the generally accepted rule of exclusive terminal addition does not hold true for additions to carbon-carbon triple bonds. Formation of considerable amounts of the α -adduct can hardly be explained in terms of the free-radical mechanism proposed for these additions⁹. Therefore, a closer study of the mechanistic aspects of the reactions leading to the several 1 : 1 adducts was made, the results of which will be presented in subsequent papers.

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.

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. In most of the NMR experiments carbon tetrachloride was used as a solvent (30–80% by volume). Experiments in this solvent, in which the concentration of the solute [for this purpose a mixture of compounds (VIa) and (VIIa), compare Table 1] was varied from 10% to 80% (by volume), revealed that within this concentration range the chemical shifts are not a function of the concentration.

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.

Gas-chromatographic analyses were made by means of F & M Gas Chro-

* 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.

matographs 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, carbowax and silicone oil columns have been used (see also ref. 2, 3 and 4).

As an example of the procedure followed experiment 11 has been described below*.

Addition of triethyltin hydride to 1-hexyne (exp. 11)

A mixture of 2.3 g (11.1 mmoles) of triethyltin hydride and 1.0 g (12.2 mmoles) of 1-hexyne was heated at 50° for 6 h. Samples were taken from this mixture and analyzed by means of GLC (~55% conversion after 6 h). The reaction mixture was left overnight at room temperature and heated at 50° for an additional period of 6 h (conversion ~85%). As appeared from the gas chromatograms the amount of adduct (XXIVb) remained almost constant after the first heating period, whereas the amount of adduct (XXVb) increased steadily.

Distillation afforded 2.3 g (72% yield) of a mixture of 1:1 adducts, boiling at 52–58°/0.06 mm, n_D^{20} 1.4822. (Found: Sn 41.2. $C_{12}H_{26}Sn$ calcd.: Sn 41.06%.)

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SUMMARY

Organotin monohydrides were brought into reaction with a variety of mono- and disubstituted ethynes. The identity of the resulting products was established by means of elementary analysis, infrared absorption spectroscopy and proton magnetic resonance spectroscopy.

In the hydrostannation of monosubstituted ethynes both α - and β -adducts are formed. Electron-withdrawing substituents favour the formation of α -adducts. In the formation of the β -adducts, as well as in the hydrostannation of disubstituted ethynes, *trans*-addition seems to be the rule.

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