

STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXXII*. SYNTHESIS OF SEVEN- AND FOURTEEN-MEMBERED TIN-CONTAINING HETEROCYCLES**

A. J. LEUSINK, H. A. BUDDING AND J. G. NOLTES

Organisch Chemisch Instituut TNO, Utrecht (The Netherlands)

(Received April 20th, 1970)

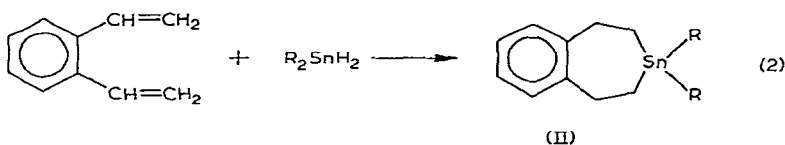
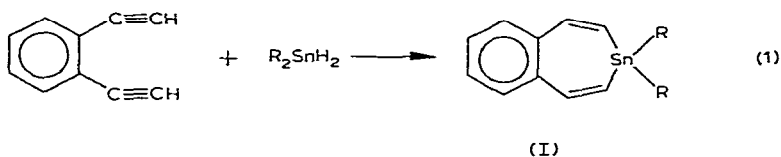
SUMMARY

Reaction of organotin dihydrides with *o*-divinyl- and *o*-diethynylbenzene affords, in addition to polymeric products, seven- and fourteen-membered tin-containing heterocycles. The structures of these compounds have been established by elemental analysis, mol.wt. determinations, IR, UV and NMR spectroscopy, and by degradation with iodine.

INTRODUCTION

Hydrostannations involving organotin dihydrides and alkadienes, alkynes or alkadiynes in general will lead to the formation of tin-containing polymers and cyclic oligomers. The latter compounds are formed in particular in reactions of organotin dihydrides with terminal dienes and diynes having the unsaturated groups in a sterical position favouring ring formation^{1,3-5}.

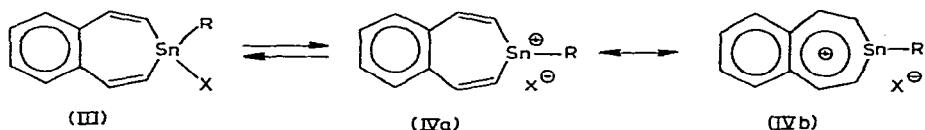
The present study, which deals with organotin hydride additions to *o*-divinyl- and *o*-diethynylbenzene, was undertaken with the aim to prepare benzostannepin (I) and its tetrahydro derivative (II) and to investigate their properties and reactions. In



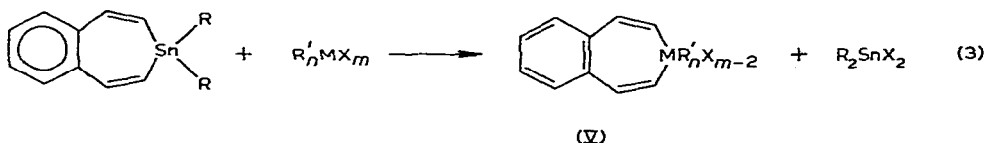
*For Part XXXI see ref. 1.

**A preliminary account of this work has appeared in print².

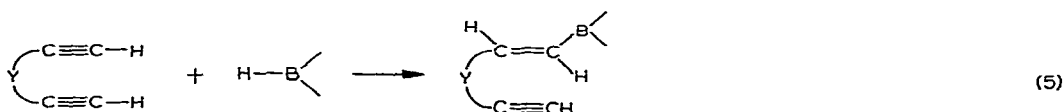
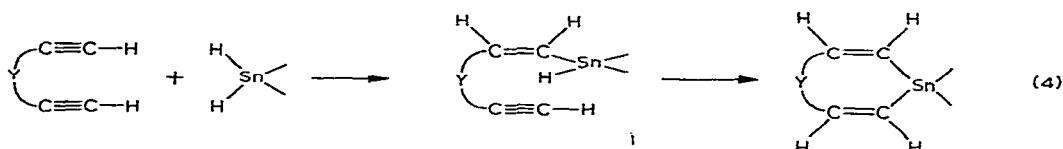
particular derivatives of type (III) are of importance since such compounds might exist under appropriate conditions as stannatropylium ions (IVb)⁵.



Furthermore, compounds of type (I) may be used for the synthesis of metal-epin systems (V) of other metals by metal-metal exchange^{6,7}:



Such a preparative route is of importance for the synthesis of metal-epin compounds which cannot be obtained by similar hydrometalations (or other routes). This is exemplified by the synthesis of 3-phenyl-3-benzoborepin from 3,3-dimethyl-3-benzostannepin⁶. Hydrostannation of acetylenic compounds proceeds by a *trans*-addition⁸, whereas hydroborations are *cis*-additions⁹. Since *trans*-addition is a prerequisite for the formation of small rings [compare eqn. (4)] hydroboration as such cannot be a route to borepin systems [compare eqn. (5)].

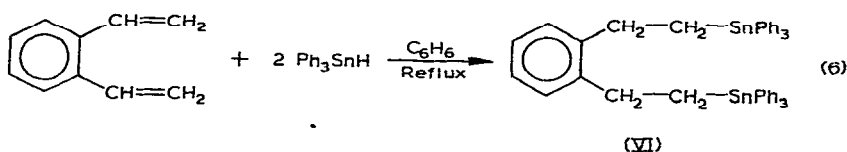


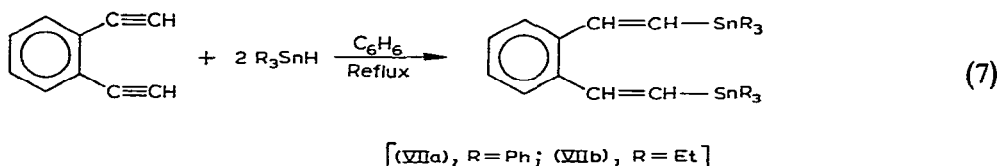
In the present paper the synthesis of cyclic oligomers from organotin dihydrides and *o*-divinyl- and *o*-diethynylbenzene is described. In subsequent papers the reactions of these compounds will be discussed.

RESULTS AND DISCUSSION

Reaction of organotin monohydrides with *o*-divinyl- and *o*-diethynylbenzene

Model reactions of organotin monohydrides with *o*-divinyl- and *o*-diethynylbenzene in a 2/1 ratio afforded the expected 2/1 addition products (VI) and (VII), respectively, in satisfactory yields (see also Table 1).

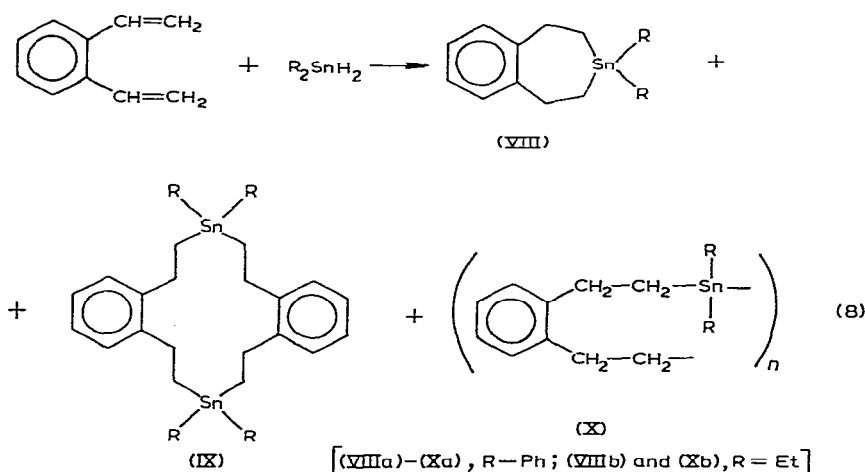




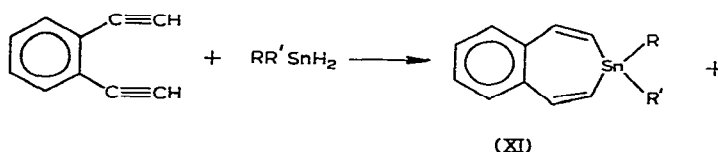
As will be discussed below compounds (VIIa) and (VIIb) are in fact mixtures of geometrical isomers.

Reaction of organotin dihydrides with o-divinyl- and o-diethynylbenzene

Reaction of diphenyltin dihydride with an equimolar amount of *o*-divinylbenzene yielded a mixture of products. Separation of this mixture afforded a compound (A) melting at about 100° (22% yield), a compound (B) melting at about 280° (15% yield) and a polymeric product (60% yield). All three compounds analysed correctly for 1/1 adducts. The absence of SnH and vinyl absorptions in the IR spectra of the crystalline products (A) and (B) excludes open chain structures with SnH and vinyl end groups for these compounds. Obviously (A) and (B) are cyclic oligomers. Molecular weight determinations revealed that (A) and (B) are the seven-membered cyclic monomer (VIIIa) and the fourteen-membered cyclic dimer (IXa), respectively.



From the reaction of diethyltin dihydride with *o*-divinylbenzene the cyclic monomer (VIIIb) and the polymer (Xb) were obtained. No attempts were made to isolate the cyclic dimer (IXb), which may have been formed as well. Reactions of organotin dihydrides with *o*-diethynylbenzene afforded the corresponding 1/1, 2/2 and polymeric adducts:



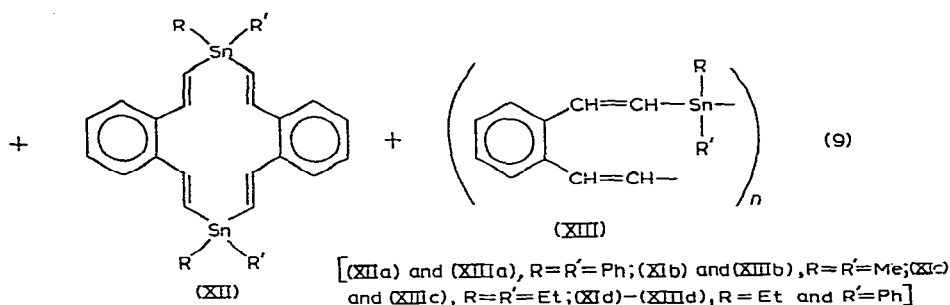


TABLE I

YIELDS, PHYSICAL CONSTANTS AND ANALYTICAL DATA OF COMPOUNDS (VI)–(XIII)

Compound		Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)			Mol. wt. found ^a (calcd.)
No.	Formula			C	H	Sn	
(VI)	C ₄₆ H ₄₂ Sn ₂	86	111–114	66.36 (66.39)	5.09 (5.09)	28.71 (28.52)	
(VIIa)	C ₄₆ H ₃₈ Sn ₂	80	^b	66.65 (66.64)	4.74 (4.72)	28.85 (28.66)	
(VIIb)	C ₂₂ H ₃₈ Sn ₂	72	^c	49.01 (48.94)	7.21 (7.09)	43.99 (43.97)	
(VIIIa)	C ₂₂ H ₂₂ Sn	22 (10) ^d	98–100	65.27 (65.23)	5.37 (5.48)	29.53 (29.30)	408, 397, 395, 392 (405.1)
(VIIIb)	C ₁₄ H ₂₂ Sn	17 (10) ^d	^e	54.32 (54.42)	7.10 (7.18)	38.22 (38.40)	290 ^f , 309 ^g (309.0)
(IXa)	C ₄₄ H ₄₄ Sn ₂	15 (11) ^d	278–281	65.69 (65.23)	5.92 (5.48)	29.10 (29.30)	797 ^g (810.2)
(Xa)	(C ₂₂ H ₂₂ Sn) _n	60	60–70			29.53 (29.30)	
(Xb)	(C ₁₄ H ₂₂ Sn) _n	75		54.56 (54.42)	7.05 (7.18)		
(XIb)	C ₁₂ H ₁₄ Sn	10 (6) ^d	41–42 ^h	51.86 (52.04)	5.00 (5.09)		273, 281, 276 ^g (277.0)
(XIc)	C ₁₄ H ₁₈ Sn	22 (17) ^d	ⁱ	55.14 (55.13)	6.08 (5.95)		298 ^g , 312 ^g (305.0)
(XId)	C ₁₈ H ₁₈ Sn	5					445 ^{g,j} (353.0)
(XIIa)	C ₄₄ H ₃₆ Sn ₂	17 (12) ^d	290–291	65.56 (65.89)	4.42 (4.52)	29.48 (29.60)	749, 802, 786 ^g (802.2)
(XIId)	C ₃₆ H ₃₆ Sn ₂	41 (25) ^d	184–186	60.90 (61.24)	5.20 (5.14)	33.61 (33.62)	700 ^g (706.1)
(XIIIa)	(C ₂₂ H ₁₈ Sn) _n	70	60–80	65.20 (65.89)	4.57 (4.52)	29.74 (29.60)	
(XIIIb)	(C ₁₂ H ₁₄ Sn) _n	80					
(XIIIc)	(C ₁₄ H ₁₈ Sn) _n	50					
(XIId)	(C ₁₈ H ₁₈ Sn) _n	50			32.63 (33.62)		

^a Mol. wt. were determined in methylene chloride (unless otherwise stated) using a Mechrolab vapor pressure osmometer. ^b Mixtures of isomers melting in the range between 100° and 145° were isolated (see also text). ^c B.p. 155° (0.001 mm), n_D^{20} 1.5682. ^d Yield (%) after extensive purification. ^e B.p. 93–98° (0.08 mm), n_D^{20} 1.5616. ^f In chloroform. ^g In benzene. ^h B.p. 76° (0.2 mm). ⁱ B.p. 96° (0.04 mm), n_D^{20} 1.5983. ^j Contaminated with some polymer (and/or dimer, see also experimental and Table 2, footnote g).

The following compounds were isolated from the reaction mixtures: $R=R'=Ph$, dimer (XIIa) and polymer (XIIIa); $R=R'=Me$ or Et , monomers (XIb) and (XIc), and polymers (XIIIb) and (XIIIc); $R=Et$ and $R'=Ph$, monomer (XIId), dimer (XIId) and polymer (XIIId). Attempts to isolate monomer (XIa) ($R=R'=Ph$) failed. No attempts were made to isolate the cyclic dimers (XIIb) and (XIIc) ($R=R'=Me$ or Et).

Yields, physical and analytical data of the compounds mentioned above are given in Table 1. Furthermore, these products have been characterized by IR, UV and NMR spectroscopy and by degradation with iodine (see below).

IR spectra

In Table 2 some characteristic absorptions of the various products obtained have been presented. The $C=C(-Sn)$ stretching vibration at about 1580 cm^{-1} only present in the spectra of the unsaturated compounds (derived from *o*-diethynylbenzene) needs no further comment. The other two IR bands mentioned in Table 2 have been found to be very useful in the characterization of the oligomeric and polymeric compounds. The spectra of all seven-membered tin-containing heterocycles

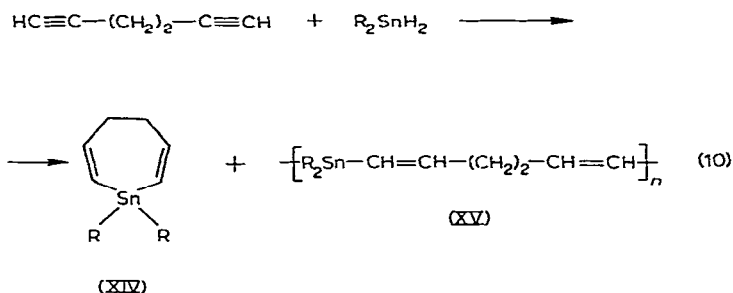
TABLE 2

IR AND UV DATA OF COMPOUNDS (VIII)–(XV)

Compound		IR ^a data (cm^{-1})			UV ^b data [$\text{nm} (\log \epsilon)$]	
No.	Type ^c	$\nu[C=C(Sn)]^d$	$\gamma[HC=CH(Sn)]^d$	780 cm^{-1} vibr. ^{d,e}	Main band ^d	Cis band ^d
(VIIIa)	7 sat.			782 vs		
(VIIIb)	7 sat.			781 vs	<i>f</i>	<i>f</i>
(IXa)	14 sat.			<i>f</i>		
(Xa)	Pol. sat.			<i>f</i>		
(Xb)	Pol. sat.			<i>f</i>		
(XIb)	7 unsat.	1582 s	<i>f</i>	781 vs	<i>f</i>	228 (4.51)
(XIc)	7 unsat.	1582 s	<i>f</i>	783 vs	<i>f</i>	230 (4.36)
(XIId)	7 unsat.	1582 s	(986 w) ^g	783 vs	<i>f</i>	224 (4.50)
(XIIa)	14 unsat.	1570 s	982 vs	(789 w)	251 (4.78)	<i>f</i>
(XIIId)	14 unsat.	1570 m	982 vs	(789 w)	252 (4.81)	<i>f</i>
(XIIIa)	Pol. unsat.	1572 m	985 m	(781 w) ^h		
(XIIIb)	Pol. unsat.	1577 m	983 s	<i>f</i>		
(XIIId)	Pol. unsat.	1571 m	984 s	(782 w) ^h		
(XIVa) ⁱ	7 unsat.	1580 vs	<i>f</i>	787 s		
(XIVc) ^j	7 unsat.	1595 vs	<i>f</i>	786 s		
(XIVe) ^k	7 unsat.	1585 vs	<i>f</i>	786 s		
(XVa) ⁱ	Pol. unsat.	1588 vs	986 s	<i>f</i>		
(XVc) ^j	Pol. unsat.	1590 vs	989 vs	<i>f</i>		
(XVe) ^k	Pol. unsat.	1590 vs	987 vs	<i>f</i>		

^aNeat or KBr pellet. ^bIn cyclohexane. ^c7: seven-membered heterocycle; 14: fourteen-membered heterocycle; pol.: polymer; sat.: saturated; unsat.: unsaturated. ^dSee text. ^eSkeletal vibration of seven-membered heterocycle (see also text). ^fEssentially no (or only very weak) absorption has been found in this region. ^gAbsorption may be due to the presence of a small amount of polymer (or dimer) in the monomer sample (see also experimental and Table 1, footnote j). ^hAbsorption may be due to the presence of a small amount of monomer present in the polymer sample (see also experimental). ⁱ $R=Ph$ (see text). ^j $R=Et$ (see text). ^k $R=Bu$ (see text).

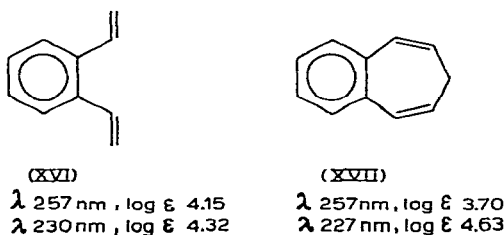
prepared so far showed an intense absorption band at about 783 cm^{-1} . Since this band is present in the spectra of both the saturated and unsaturated seven-membered heterocycles, but absent in the spectra of the corresponding fourteen-membered heterocycles and polymers, we tentatively assign this absorption to a skeletal vibration of the seven-membered ring system. The same absorption (although somewhat weaker) is present in the IR spectra of 1-stanna-2,6-cycloheptadienes (XIV), but again absent in the spectra of the corresponding polymers (XV). The latter compounds have been prepared by one of us some years ago⁴:



A second band which has been used in the characterization of the unsaturated compounds is the out-of-plane vibration of *trans*-ethylene at about 985 cm^{-1} . This absorption is present in compounds (VII), (XII), (XIII) and (XV), but absent in the seven-membered heterocycles (XI) and (XIV) which inevitably must have an all-*cis* structure.

UV spectra

As discussed by Dale and Hubert¹⁰ the intensity relationship existing between the main (fundamental) band, occurring at longest wavelengths, and the *cis* (first overtone) band, occurring at shorter wavelengths, in conjugated polyene systems also holds for polyene systems containing an *ortho*-linked benzene ring. In general compounds with a *trans*-shape show an intense main band and a weaker *cis* band, whereas the intensities of these bands are reversed in compounds with a V-shaped *cis* structure. For example:



As can be seen from Table 2 the seven-membered unsaturated heterocycles showed a strong *cis* band at 224–230 nm, whereas in the spectra of the corresponding fourteen-membered heterocycles a strong main band at 251–252 nm is present. This further supports the structural assignments.

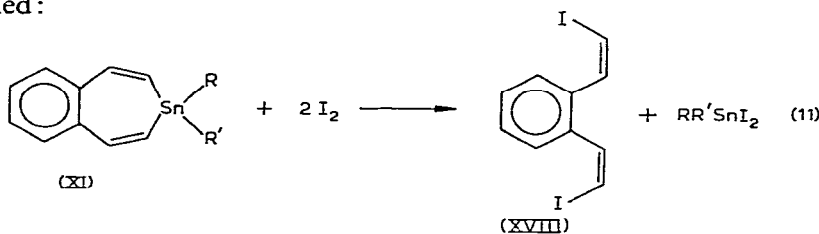
NMR spectra

Conclusive proof for the *cis*- and *trans*-structures of the unsaturated seven- and fourteen-membered heterocycles is given by their NMR spectra (Table 3). Both chemical shifts and coupling constants of the olefinic protons are completely in accord with previous results¹¹.

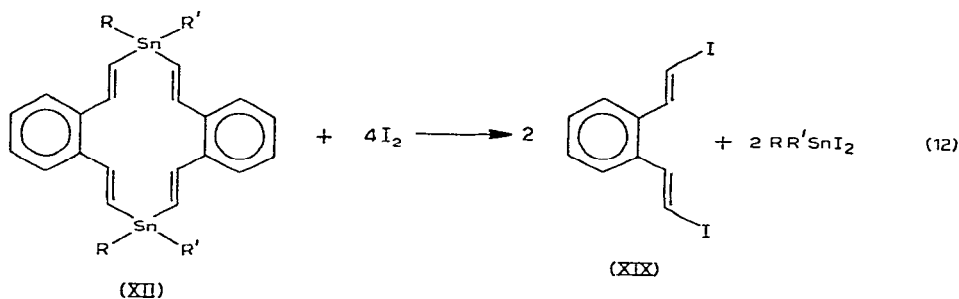
The NMR spectrum of the 2/1 adduct (VIIb) revealed that this product contained mainly the *cis,trans* and *trans,trans* isomers. In the spectrum *cis* protons appear at 6.25 and 7.73 ppm and *trans* protons at 6.64, 7.07 (?), 6.58 and 7.19 ppm in a ratio of about 1/1/1/1/3/3. Obviously the signals at 6.25/7.73 ppm (*cis*) and 6.64/7.07 ppm (*trans*) arise from the *cis,trans* adduct, while the signals at 6.58/7.19 ppm (*trans*) arise from the *trans,trans* adduct (see also Table 3; ratio *cis,trans*/*trans,trans* about 40/60, ratio *cis,trans*/*trans,trans* as found by degradation with iodine: 46/54). In the spectrum of (VIIa) *cis* protons were found at 6.53 and 7.87 ppm, which as appeared from their intensity obviously arise from the *cis,trans* adduct (degradation by iodine showed that mainly the *cis,trans* adduct was present).

Degradation by iodine

As will be discussed in detail in a next paper⁷ the ethenyl-tin bonds in the products from organotin hydrides and *o*-diethynylbenzene are easily cleaved by iodine yielding organotin iodides and (2-iodovinyl)benzene compounds with retention of configuration. Thus, upon reacting the seven-membered heterocycles with two equivalents of iodine *o*-bis(*cis*-2-iodovinyl)benzene and organotin diiodides were obtained:

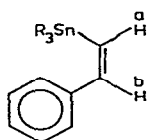


The corresponding fourteen-membered heterocycles yielded *o*-bis(*trans*-2-iodovinyl)benzene:

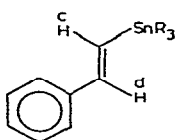


Compounds (XVIII) and (XIX) have been isolated and characterized⁷.

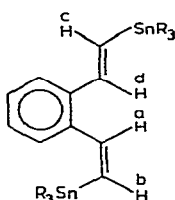
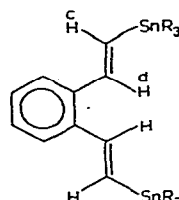
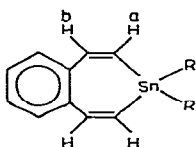
Reaction of iodine with fractions of (VIIa) and (VIIb), which according to NMR spectroscopy contain considerable amounts of the *cis,trans* adduct, afforded in general, in addition to the organotin iodide, three compounds (detected by GLC): the *cis,cis*-diiodide, the *trans,trans*-diiodide and an unknown compound with a



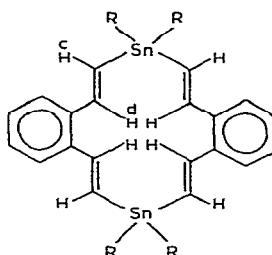
(XXI)



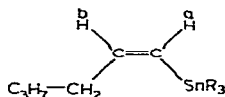
(XXII)

(VII) (*cis,trans*)(VII) (*trans,trans*)

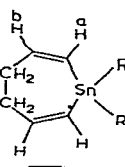
(XI)



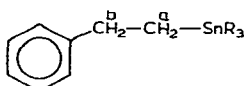
(XII)



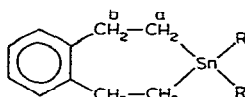
(XXIII)



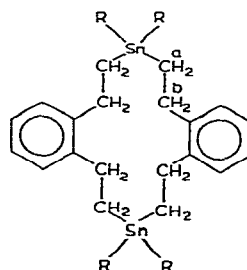
(XIV)



(XXIV)

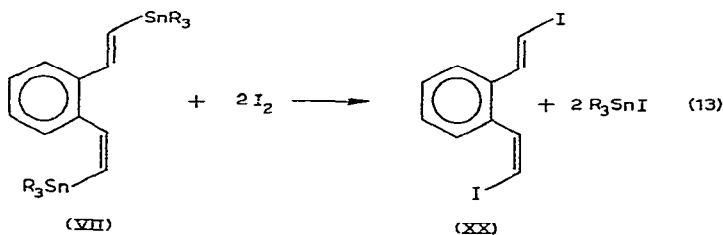


(VIII)



(IX)

retention time between that of the *cis,cis*-diiodide and that of the *trans,trans*-diiodide. Obviously this unknown compound is the *cis,trans*-diiodide originating from degradation of the *cis,trans*-ditin adduct:



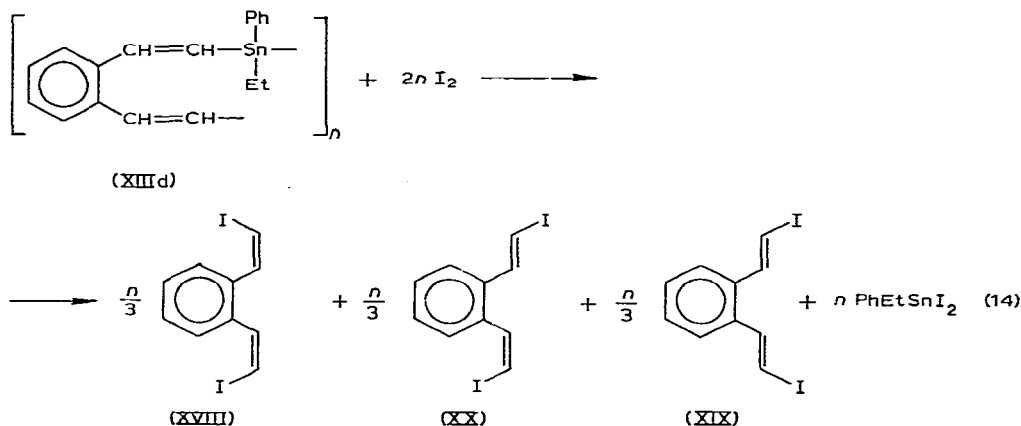
The polymeric products of type (XIII) also reacted readily with iodine giving the diiodides (XVIII), (XIX) and (XX) in varying ratios. For example, degradation of the polymer (XIIIId) with iodine revealed that this polymer contained *cis,cis*-, *cis,trans*- and *trans,trans*-structural elements in a ratio of about 1/1/1:

TABLE 3

NMR DATA OF COMPOUNDS (VII)–(IX), (XI), (XII), (XIV) AND (XXI)–(XXIV)^a

Compound		Chemical shifts (ppm) ^b				Coupling constants (Hz)			
No.	R	δH_a	δH_b	δH_c	δH_d	J_{ab}	J_{cd}	J_{ax}^c	J_{bx}^c
(XXI)	Ph ^d	d 6.43	d 7.80			13.4		~70	~164
	Et ^d	d 6.15	d 7.62			13.7		57.0/59.5	132.5/138
(XXII)	Ph			s 7.02	s 7.02				
	Et ^d			b 6.83	b 6.83				
(VII) (c, tr)	Ph	d 6.53	d 7.87			13.5			
	Et	d 6.25	d 7.73	d 6.64	d 7.07	13.6	19.4		
(VII) (tr, tr)	Et			d 6.85	d 7.19		19.4		
(XI)	Me	d 6.30	d 7.46			13.8		79.0/83.0	147.0/154.0
(XII)	Ph			d 6.90	d 7.70		19.0		
(XXIII)	Ph ^d	^d 6.11	^d 6.75			12.0		~92?	~176?
	Et ^d	^d 5.70	^d 6.49			12.5		~73	~143
(XIV)	Ph	d 6.22	m 6.93			12.7		88.5/92.5	~167
	Et	d 5.96	m 6.78			12.8		85.0/89.0	~150
	Bu	d 5.95	m 6.74			12.6		85.5/89.5	~150
(XXIV)	Ph ^e	^t 1.80	^t 3.00			8.2 ^g		~54	~54
(VIII)	Ph	^t 1.64	^t 3.15			6.9 ^g		51.0/53.5	85.5/89.5
(IX)	Ph	m 1.65	m 3.04					~101	~56

^aSolvent: CCl₄ or CDCl₃. ^bDownfield from TMS internal; s: singlet; d: doublet; t: triplet; m: multiplet; b: unresolved broad signal. ^cCoupling constants with ¹¹⁷Sn and ¹¹⁹Sn isotopes, respectively. ^dSee also ref. 11. ^eSee also ref. 1. ^f"Distorted triplet", in fact multiplet of AA'BB' system. ^gDistance between the (three) main lines of the multiplet (see footnote f).



EXPERIMENTAL

General

All reactions involving organotin hydrides were carried out in an atmosphere of dry oxygen-free nitrogen. Liquids were handled by the syringe technique. 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.

IR and UV spectra, which were run by Miss L. Veldstra, were recorded using a Perkin-Elmer spectrophotometer type Infracord 137, a Grubb Parsons Spectrometer and a Beckman DU UV spectrophotometer. NMR spectra, which were run by Miss L. Veldstra and Mr. J. W. Marsman, were recorded using Varian Associates HR-100 A and HA-100 NMR spectrometers. Gas-chromatographic analyses, which were performed by Mrs. G. G. Versluis-de Haan and Mr. J. W. Marsman, were made by means of an F&M Gas Chromatograph Model 500. Molecular weights were determined by Mr. C. W. Dekker using a Mechrolab Vapor Pressure Osmometer.

Starting materials

o-Divinylbenzene was synthesized from *o*-xylene, via *o*-bis(bromomethyl)benzene, *o*-bis[(ethoxycarbonyl)methyl]benzene and *o*-bis(2-hydroxyethyl)benzene according to published methods^{12,13}. *o*-Diethynylbenzene was obtained by bromination of *o*-divinylbenzene followed by dehydrobromination of the tetrabromo product^{14,15}.

Triphenyl-, triethyl-, diphenyl- and diethyltin hydrides were prepared from the corresponding chlorides by reduction with lithium aluminium hydride in diethyl ether. Ethylphenyltin dihydride (b.p. 56–58°/12 mm, n_D^{20} 1.5544) was obtained by the same procedure from ethylphenyltin diiodide (prepared from triphenylethyltin and iodine). The LiAlH_4 -reduction of dimethyltin dichloride to the dihydride was carried out in dioxane; in this particular case the resulting reaction mixture was not treated with water as usual, but the tin hydride was removed from the mixture by distillation at reduced pressure (bath temp. 60°, pressure 160 mm, CO_2 /acetone trap).

Reaction of diphenyltin dihydride with o-divinylbenzene

A solution of diphenyltin dihydride (24.1 g, 88 mmol) and *o*-divinylbenzene (11.4 g, 88 mmol) in benzene (600 ml) was refluxed for 10 h. The benzene was removed from the mixture and the residue was heated at 100° for 6 h. After these heating periods the reaction was complete as appeared from the disappearance of the $\nu(\text{Sn-H})$ absorptions around 1850 cm^{-1} in the IR spectrum. Crystallization of the resulting product from benzene afforded 5.2 g (14.6%) of a high-melting solid (m.p. $\sim 280^\circ$) and a polymeric residue (from the filtrate). The high-melting product was recrystallized from DMF and subsequently from benzene yielding 4 g (11.2%) of pure dimer (IXa), m.p. 278–281°.

The polymeric residue was heated at 160–170° at 0.1 mm and 8 g (22.4%) of a sublimate was obtained. After a second sublimation this product (5.6 g, 15.7%) melted at about 100°. Purification by column chromatography (Al_2O_3 , eluent methanol, removal of a very small amount of tetraphenyltin), recrystallization (three times from petroleum ether 60–80° and twice from ethanol), sublimation (two times) and recrystallization (from ethanol) furnished pure monomer (VIIIa), m.p. 98–100°.

Reaction of diphenyltin dihydride with o-diethynylbenzene

A solution of diphenyltin dihydride (21.2 g, 77 mmol) and *o*-diethynylbenzene (9.72 g, 77 mmol) in benzene (900 ml) was refluxed for 16 h. After removal of the greater part of the solvent from the reaction mixture a solid separated from the

solution. Filtration afforded 5.3 g (17.1%) of white crystals, melting at $\sim 270^\circ$. After recrystallization (once from toluene, twice from DMF) almost pure dimer (3.7 g, 11.9%, m.p. $282\text{--}285^\circ$) was obtained. A small portion of this product was recrystallized from chloroform yielding pure dimer (XIIf), m.p. $290\text{--}291^\circ$.

Reaction of ethylphenyltin dihydride with o-diethynylbenzene

In the same way as described above equimolar amounts (68 mmoles) of ethylphenyltin dihydride and *o*-diethynylbenzene were heated in benzene (450 ml). The residue obtained after removal of the solvent was treated with petroleum ether $40\text{--}60^\circ$, yielding 9.8 g (41%) of a solid melting at 180° and a polymeric residue. The product melting at 180° was purified by repeated crystallization from propanol affording 6.0 g (25%) of pure dimer (XIId), m.p. $184\text{--}186^\circ$.

The polymeric residue was treated with hot methanol and the methanolic extract was evaporated giving 1.3 g (5.4%) of an oil, which according to IR and UV spectroscopy, iodine degradation and mol.wt. determination consisted of monomer (XId) contaminated with some polymer (and/or dimer).

Reaction of dialkyltin dihydrides with o-diethynylbenzene

The best results were obtained by the following working-up procedure. After the reaction is complete (IR) the solvent (benzene) is removed by distillation and the residue is added dropwise to a 4/1 mixture of methanol/petroleum ether $60\text{--}80^\circ$ resulting in the formation of two layers. The supernatant liquid is decanted and the solvents are removed from both solutions by distillation giving a low and a high molecular weight product. The low molecular weight product is fractionated affording almost pure monomer. The monomeric product from dimethyltin dihydride (XIb) is subsequently recrystallized from methanol. The diethyltin monomer (XIc) is purified by a second distillation.

ACKNOWLEDGEMENTS

The authors are much indebted to Professor G. J. M. van der Kerk for valuable suggestions and active interest in the present subject.

Part of this work has been sponsored by the Air Force Materials Laboratory, Research and Technology Division, AFSC, under Contract AF 61(052)-218 through the European Office of Aerospace Research, USAF.

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