Journal of Organometallic Chemistry, 78 (1974) 385—393

BASE-CATALYSED DISPROPORTIONATION AND ADDITION REACTIONS OF HEXAALKYLDITINS*

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(Received April 16th, 1974)

Summary

Under polar conditions asymmetric hexaalkylditins, $R_3SnSnR'_3$, disproportionate rapidly at room temperature to give the symmetrical ditins R_6Sn_2 and R'_6Sn_2. The equilibrium constants observed for a series of such reactions (R = Me; R' = Et, Pr, Bu, i-Bu) point to a predominance of steric rather than inductive effects.

Hexaalkyl-ditins (and -digermanes) also react readily under polar conditions with carbon—carbon triple bond systems as well as with diethyl azodicarboxylate.

Introduction

When heated, hexaorgano-ditins and -digermanes do not dissociate into free radicals. For example, 1,1,1-trimethyl-2,2,2-triethylditin can be distilled at 235° without disproportionation. Furthermore, a 1/1 mixture of hexamethylditin and hexaethylditin remains unaltered when heated for 25 h at temperatures up to 150° [2].

It has been observed recently that with organodigermanes (M, M′ = Ge; R = Et) reaction 1 proceeds instantaneously at room temperature in HMPT (hexamethylphosphoric triamide) solution in the presence of a catalytic amount of base [3]. Studies of the reactions of organoditins under polar conditions are discussed below.

$$Me_6M_2 + R_6M'_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2Me_3MM'R_3 \qquad (1)$$

$(M, M' = Ge, Sn;\ R = Et)$

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* A preliminary paper has already appeared [1].

TABLE 1

REACTION BETWEEN EQUIMOLAR AMOUNTS OF Me_6Sn_2 AND Et_6Sn_2 AT ROOM TEMPERATURE
Concentration of reactants 0.5 mmol/ml

Solvent	Catalyst (5 mole %)	Time (h)	$Me_3SnSnEt_3$ [a] (%)
THF		5	0
THF	AIBN [b]	3	0
THF	MeMgBr	0.5	52
MeCN		72	0
MeCN	MeONa	48	51
HMPT		0.1	~40
HMPT	MeMgBr	0.3	51

[a] Determined by quantitative GLC analysis. [b] 2,2'-Azobis(isobutyronitrile); reaction temperature 60°.

Results and discussion

Disproportionation reactions

In Table 1 the results of reactions of the type shown in equation 1 (M, M' = Sn; R = Et) are collected. In THF or acetonitrile solutions at room temperature reaction takes place only in the presence of a catalytic amount of base (e.g., MeMgBr, MeONa), whereas in the strongly basic solvent HMPT reaction proceeds even without a catalyst.

The equilibrium constant K_1 was found to be effectively the same in THF, MeCN and HMPT, viz. $K(\text{THF}) = 0.23 \pm 0.02$; $K(\text{MeCN}) = 0.24 \pm 0.02$; $K(\text{HMPT}) = 0.25 \pm 0.02$; this value of K_1 implies an almost random distribution of the trimethyltin and triethyltin groups ($K_1 = 0.25$). In contrast, the equilibrium constant K_1 for the base-catalysed disproportionation between hexamethyldigermane and hexaethyldigermane in HMPT was found to be 0.12 [3].

The equilibrium constants determined for reaction 1 with M = Sn and R = Et, Pr, Bu, i-Bu (Table 2) indicate that the more different the steric bulk of the two trialkyltin groups the more the distribution deviates from randomness, with preference for the mixed ditin species. Thus, steric rather than inductive effects seem to be of dominant importance.

As demonstrated by the synthesis of some new compounds of the type Me_3SnSnR_3 (Table 3), reaction 1 offers an attractive preparative route to mixed-substituted ditins. Preliminary experiments showed that this reaction also occurs (in HMPT solution) with M = Si, Ge and M' = Ge, Sn (R = Me) to give the corresponding mixed Group IV metal—metal bonded compounds. With the sys-

TABLE 2

EQUILIBRIUM CONSTANTS FOR REACTION 1 (M = Sn) IN THF AT ROOM TEMPERATURE
Catalyst: 5—10 mole percent MeMgBr

R	K_1	σ^* [a]	E_s [b]
Et	0.22 ± 0.02	−0.100	−0.07
Pr	0.13 ± 0.02	−0.115	−0.36
Bu	0.18 ± 0.02	−0.130	−0.39
i-Bu	0.020 ± 0.005	−0.125	−0.93

[a] σ^*: polar substituent constant [4]. [b] E_s: steric substituent constant [4].

TABLE 3

PHYSICAL CONSTANTS AND YIELDS OF SOME NEW ORGANOTIN COMPOUNDS

Compound [a]	B.p. (°C/mmHg)	n_D^{20}	Yield [b] (%)
$Me_3SnSnEt_3$ [c]	62—64/0.3	1.5378	54
$Me_3SnSnPr_3$	69—70/0.1	1.5282	44
$Me_3SnSnBu_3$	106—108/0.3	1.5079	66
Me_3SnSn-i-Bu_3	78—80/0.1	1.5217	85
I (M = Sn, R = Me)	130—131 [d]		47
I (M = Sn, R = Et)	59—60 [d]		82
I (M = Ge, R = Me)	121—122 [d]		25
II (R = Ph)	95—96/0.2	1.5670	25
III	122—125 [d, e]		11
VI	111—115 [d, f]		
VIII	85—90 [d]		80

[a] Satisfactory analysis data have been obtained for all compounds (see Experimental). [b] Based on the amount of ditin consumed. [c] Lit. [2] b.p. 235°. [d] M.p. [e] A freshly prepared sample showed a melting range, 130—210°, whereas on remelting a sharp melting point of 122—125° was observed. [f] B.p. 132—135°/0.5 mmHg.

tem Me_6Sn_2/Me_6Pb_2 in THF (catalyst 5% MeMgBr) only decomposition of the Me_6Pb_2 into Me_4Pb and metallic lead was observed, the Me_6Sn_2 remaining unaltered. In HMPT and without a catalyst the latter system immediately gave, as shown by PMR spectroscopy, equimolar amounts of Me_6Sn_2 and Me_4Sn, together with tetramethyllead and lead. These results may be explained by the intermediate formation of $Me_3SnPbMe_3$, which decomposed according to reaction 2.

$$\mathrm{Me_3SnPbMe_3} \rightarrow \mathrm{Me_4Sn} + \begin{array}[t]{c}[\mathrm{Me_2Pb}]\\ \downarrow \\ \mathrm{Me_4Pb + Pb}\end{array} \qquad (2)$$

Addition reactions

In view of the appreciably enhanced reactivity of the metal—metal bond under polar conditions, we decided to see whether addition of ditins, and digermanes to unsaturated systems can be brought about under similar conditions. Information on such addition reactions has previously been limited to the reaction of hexamethylditin with perfluoro-olefins and -acetylenes under free radical conditions [5, 6].

Hexaalkyl-ditins and -digermanes were found to react smoothly with carbon—carbon triple bond systems in HMPT solution and in the presence of a catalytic amount of base (MeONa, MeLi, Li) to give exclusively the corresponding *trans*-adducts. Reaction of hexamethylditin with diphenylacetylene in HMPT solution, catalysed by 5 mole percent of sodium methoxide gave, after 6 h at 50° and subsequently 60 h at room temperature, about 70% of *trans*-1,2-bis(trimethylstannyl)-1,2-diphenylethylene (I, M = Sn, R = Me)* (reaction 2). The *trans*-structure of the adduct was confirmed by bromine cleavage, which gave ex-

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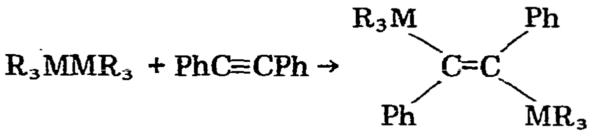
* Hexamethylditin is completely stable on heating in HMPT for 5 h at 50° in the presence of 5 mole percent of MeONa. Under more drastic conditions, however, considerable decomposition occurs to give, among other products, Me_4Sn.

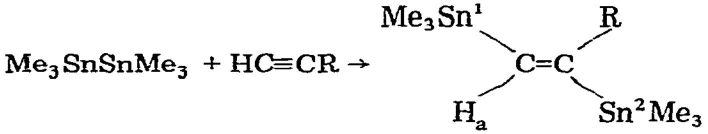


$$R_3MMR_3 + PhC{\equiv}CPh \rightarrow (R_3M)(Ph)C{=}C(Ph)(MR_3) \qquad (3)$$

(M = Sn; R = Me, Et; M = Ge; R = Me)

clusively α,α′-dibromo-*trans*-stilbene (isolated), and by cleavage with sodium methoxide in a HMPT/methanol mixture, which gave exclusively *trans*-stilbene (GLC). Addition could only be accomplished in HMPT and in the presence of a catalytic amount of base. Attempts to perform reaction 3 (M = Sn; R = Me) in THF, methanol or acetonitrile solution in the presence of sodium methoxide at 50° failed.

Although slightly less reactive than hexamethylditin, hexaethylditin and hexaethyldigermane similarly gave the adducts I (M = Sn, R = Et and M = Ge, R = Me). The *trans*-adduct was also obtained with phenylacetylene, whereas with 1-hexyne only a very small amount of reaction occurred.



$$Me_3SnSnMe_3 + HC{\equiv}CR \rightarrow (Me_3Sn^1)(H_a)C{=}C(R)(Sn^2Me_3) \qquad (4)$$

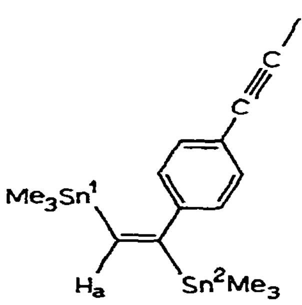
(R = Bu, Ph) (II)

Diphenylbutadiyne reacted with hexamethylditin in either 1/1 or 1/2 ratio to give 1,4-diphenyl-1,2,3,4-tetrakis(trimethylstannyl)-1,3-butadiene (III).

$Ph{-}C(Sn^2Me_3){=}C(Sn^1Me_3){-}C(SnMe_3){=}C(SnMe_3)Ph$

(III)

Reactions of hexamethylditin with both *para-* and *ortho*-diethynylbenzene gave rather complex product mixtures. By repeated distillation and/or preparative GLC products IV—VI and product VII, respectively, were isolated (cf. Table 3). Compound V was presumably formed by partial hydrolysis of adduct IV during the work-up. Further studies are required in order to decide whether compounds VI and VII are formed in a similar way from the *cis*-bis(tin) adduct.



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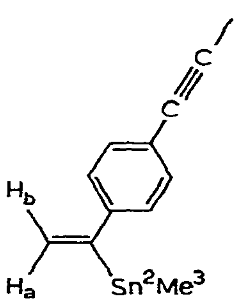

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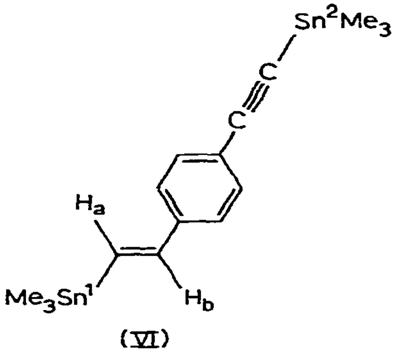

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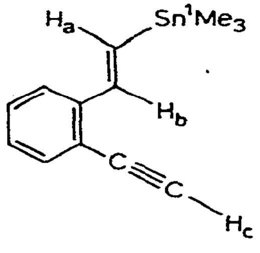


(VII)

Conclusive evidence for structures I—VII is given by their PMR spectra (Table 4). Both the chemical shifts and the coupling constants of the olefinic protons are completely in line with previous results [7].

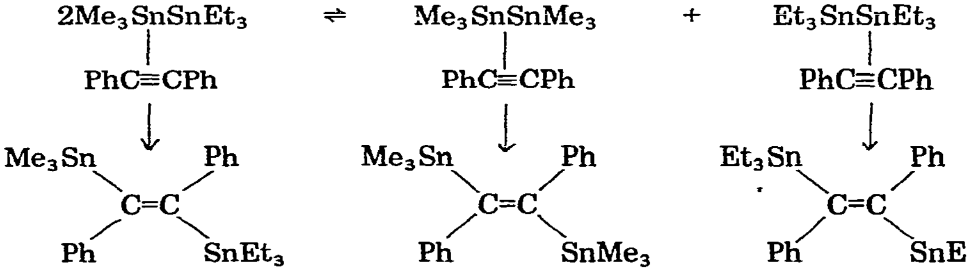
With diethyl acetylenedicarboxylate and with cyanoethyne side-reactions occurred leading to a complete degradation of the acetylenic compounds and consumption of only a few percent of the ditin (GLC). With ethoxyethyne no reaction was observed.

Attempts to perform addition of hexaalkylditins to carbon—carbon double bonds (styrene, *trans*-stilbene, 2,3-dimethylbutadiene), carbon—oxygen double bonds (benzaldehyde, acetophenone, benzophenone) and carbon—nitrogen double bonds (benzalaniline) failed. Reaction of hexamethylditin with phenyl isocyanate resulted only in trimerisation of the latter compound.

With nitrogen—nitrogen double bond systems, no reaction was observed between hexamethylditin and azobenzene, but reaction of this ditin with diethyl azodicarboxylate in HMPT proceeded smoothly, even without a catalyst, to give 1,2-bis(trimethylstannyl)diethyl-1,2-hydrazinedicarboxylate (eqn. 5).

$$Me_6Sn_2 + EtOOC{-}N{=}N{-}COOEt \rightarrow \underset{\text{(VIII)}}{Me_3Sn{-}N(COOEt){-}N(COOEt)SnMe_3} \qquad (5)$$

An illustrative example of both the disproportionation reaction and the addition reaction of ditins under polar conditions involves the reaction of 1,1,1-trimethyl-2,2,2-triethylditin with diphenylacetylene, which gave a mixture of all three expected adducts (GLC, PMR). In such a reaction that had not been allowed to go to completion, all three ditins were observed by GLC in a ratio corresponding with an equilibrium constant of 0.23 (eqn. 6). This implies that the rate of ditin addition is equal to or lower than the rate of equilibration.



(6)

TABLE 4

PMR DATA OF COMPOUNDS I—VIII [a]

Compound		Chemical shift (ppm) [b]					Coupling constant (Hz) [c]			
		δ(CH$_3$—Sn^1)	δ(CH$_3$—Sn^2)	δH_a	δH_b	δH_c	J_{ab}	J_{ax}	J_{ay}	J_{bx}
I	(M = Sn, R = Me)	−0.26								
I	(M = Ge, R = Me)	(−0.24) [d]								
II	(R = Ph)	+0.28	+0.02	6.61 s				98	97	
III		+0.12	−0.08							
IV		+0.13	−0.10	6.49 s		2.94 s		~100	~100	
V			+0.22	5.43 d	5.98 d	2.94 s	2.5	68		140
VI		+0.21	+0.35	6.82 b	6.82 b			~ 74		~ 74
VII		+0.23		6.84 d	7.34 d	3.20 s	19.4	80		74
VIII		+0.32								

[a] Solvent CCl$_4$ or CDCl$_3$. [b] Downfield from TMS; s, singlet; d, doublet; b, unresolved broad signal. [c] Coupling constants with ^{117}Sn, x referring to Sn^1, y referring to Sn^2. [d] (CH$_3$—Ge).

Mechanistic considerations

Both the disproportionation of ditins and the addition of ditins to unsaturated systems proceed exclusively under strongly polar conditions. The reaction rates are markedly enhanced by catalytic amounts of base (MeMgBr, MeONa). Similar to the anlogous reaction of digermanes [3] the disproportionation reaction of ditins may be explained by a nucleophilic attack of a trialkyltin moiety on the tin—tin bond (eqns. 8—10). The presence of a few percent of tetramethyltin (GLC, PMR) in the reaction mixtures (MeMgBr catalysis) is in accord with this picture (eqn. 7). A similar cleavage of hexaphenylditin by ethylmagnesium bromide has been reported by Creemers [8].

$$\mathrm{MeMgBr + Me_3SnSnMe_3 \rightarrow Me_4Sn + Me_3SnMgBr} \qquad (7)$$

$$\mathrm{Me_3SnMgBr + R_3SnSnR_3 \rightleftharpoons Me_3SnSnR_3 + R_3SnMgBr} \qquad (8)$$

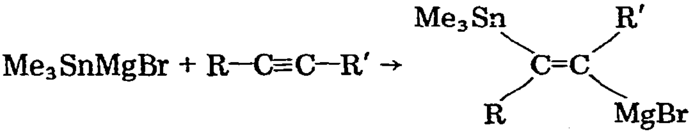
$$\mathrm{R_3SnMgBr + Me_3SnSnMe_3 \rightleftharpoons Me_3SnSnR_3 + Me_3SnMgBr} \qquad (9)$$

$$\mathrm{Me_3SnSnMe_3 + R_3SnSnR_3 \rightleftharpoons 2Me_3SnSnR_3} \qquad (10)$$

In the strongly basic solvent HMPT reaction 10 proceeds even without a catalyst. Conductivity measurements showed no appreciable dissociation of ditins in this solvent, e.g. molar conductance $\Lambda_m(\mathrm{Me_6Sn_2}) = 0.01$ ohm^{-1}cm^2 mol^{-1} (0.01 mole l^{-1} in HMPT). Therefore, in HMPT an S_N2 (cyclic) mechanism seems more plausible, as compared with an S_N2 (open) mechanism in THF solution and in the presence of base catalysts.

The addition of tin—tin bonds to carbon—carbon triple bonds likewise requires strongly polar conditions (HMPT) and a base catalyst. The reaction rate decreases in the order PhC≡CPh > PhC≡CH > BuC≡CH ≫ EtOC≡CH (unreactive). These features point to a nucleophilic attack of a trialkyltin group on carbon [9] (eqns. 11—13).

$$\mathrm{MeMgBr + Me_3SnSnMe_3 \rightarrow Me_4Sn + Me_3SnMgBr} \qquad (11)$$



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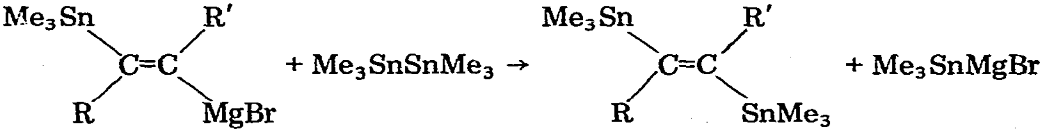

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Experimental

All reactions were performed in rigorously dried glass apparatus in an atmosphere of dry, oxygen-free nitrogen. Liquids were handled by the syringe technique. Unless otherwise indicated the starting materials were prepared according to published procedures or purchased. All materials were distilled in a nitrogen atmosphere before use.

Recording of the PMR spectra, GLC analyses, molecular weight determinations and element analyses were carried out within the Department of Physical-Organic and Analytical Chemistry under the supervision of Dr. A. Mackor, at the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

Reaction of Me_6Sn_2 with Et_6Sn_2 in THF in the presence of 5 mole percent of MeMgBr

A standard solution was prepared of 0.42 ml (0.65 g; 2.0 mmol) of Me_6Sn_2, 0.60 ml (0.82 g; 2.0 mmol) of Et_6Sn_2, 0.175 g of toluene (internal standard) and 2.80 ml of THF. GLC analysis confirmed the presence of 0.51 mmol of Me_6Sn_2 and 0.53 mmol of Et_6Sn_2 per ml of standard solution. To 1 ml of this standard solution was added in one portion 17.0 μl of a 1.5 *N* solution of MeMgBr in THF. GLC analysis of a sample taken after 0.5 h at room temperature demonstrated the presence of 0.248 mmol of Me_6Sn_2, 0.262 mmol of Et_6Sn_2 and 0.536 mmol of $Me_3SnSnEt_3$. Within experimental error (2—5%) identical results were obtained after 3 h at room temperature. The figures given in Tables 1 and 2 were obtained in a similar way, each figure being the average value of three measurements.

Synthesis of Me_3SnSnR_3 (R = Et, Pr, Bu, i-Bu)

A solution of Me_6Sn_2 (2.46 g; 7.5 mmol) and Et_6Sn_2 (3.09 g; 7.5 mmol) in 15 ml of THF was treated with 255 μl of a 1.5 *N* solution of MeMgBr in diethyl ether. After standing overnight 5 ml of a saturated aqueous solution of NH_4Cl were added, the organic layer was separated and the aqueous phase was extracted twice with diethyl ether. Fractionation gave 1.6 g (58%) of $Me_3SnSnEt_3$ (GLC one single peak).

In a similar way $Me_3SnSnPr_3$, $Me_3SnSnBu_3$ and $Me_3SnSn\text{-i-}Bu_3$ were prepared.

trans-1,2-Bis(trimethylstannyl)-1,2-diphenylethylene

To a solution of 1.78 g (10 mmol) of diphenylacetylene, 3.28 g (10 mmol) of Me_6Sn_2 and 214.4 mg of toluene (internal standard) were added 120 μl of a sodium methoxide solution, prepared by dissolving 0.5 g of sodium in 5 ml of methanol (5 mole percent of catalyst). GLC analysis after 3 h at 50° and subsequently 60 h at room temperature showed that 63% of the Me_6Sn_2 had been converted. After addition of another 5 mole percent of catalyst and additional heating for 3 h at 50°, 72% of Me_6Sn_2 had been converted. The white crystalline solid formed was separated by filtration, washed with pentane and dried, to give 1.7 g (47%, based on the amount of Me_6Sn_2 converted) of *trans*-1,2-bis(trimethylstannyl)-1,2-diphenylethylene; m.p. 130—131°. (Found: C, 47.4; H, 5.6; Sn, 47.1. $C_{20}H_{28}Sn_2$ calcd.: C, 47.49; H, 5.58; Sn, 46.93%.)

In a similar way were prepared: *trans*-1,2-bis(triethylstannyl)-1,2-diphenylethylene (82% yield) (found: C, 53.1; H, 6.6; Sn, 40.8. $C_{26}H_{40}Sn_2$ calcd.: C, 52.93; H, 6.82; Sn, 40.23%.); *trans*-1,2-bis(trimethylgermyl)-1,2-diphenylethylene (25% yield) (found: C, 58.3; H, 6.8; mol. wt. 410. $C_{20}H_{28}Ge_2$ calcd.: C, 58.08; H, 6.82%; mol. wt. 413.6); *trans*-1,2-bis(trimethylstannyl)phenylethylene (25% yield) (found: C, 39.9; H, 5.7; Sn, 53.3. $C_{14}H_{24}Sn_2$ calcd.: C, 39.13; H, 5.63; Sn, 55.24%.); 1,4-diphenyl-1,2,3,4-tetrakis(trimethylstannyl)-

1,3-butadiene (11% yield) (found: C, 39.3; H, 5.3; mol. wt. 865. $C_{18}H_{46}Sn_4$ calcd.: C, 39.22; H, 5.41%; mol. wt. 858).

1,2-Bis(trimethylstannyl)diethyl-1,2-hydrazinedicarboxylate

A mixture of 0.82 g (2.5 mmol) of Me_6Sn_2, 0.44 g (2.5 mmol) of diethylazodicarboxylate, 0.9 ml of THF and 0.1 ml of HMPT was heated for 20 h at 80°. According to GLC analysis 83% of Me_6Sn_2 was consumed. The solvents and residual starting materials were evaporated in high vacuo to give a white solid, which after washing with pentane and drying in vacuo analyzed correctly for the title compound VIII; m.p. 85—90° (yield 0.88 g, 80%). (Found: C, 28.6; H, 5.6. $C_{12}H_{28}O_4N_2Sn_2$ calcd.: C, 28.73; H, 5.63%.)

Reaction of Me_6Sn_2 with para-diethynylbenzene

A mixture of Me_6Sn_2 (2.46 g, 7.5 mmol) and *para*-diethynylbenzene (0.935 g, 7.5 mmol) in 4.5 ml of HMPT was heated for 24 h at 70° in the presence of a shred of metallic lithium (about 10 mole percent). According to GLC analysis 93% of Me_6Sn_2 was consumed. The reaction mixture was diluted with 10 ml of diethyl ether/benzene (1/1) and treated with 5 ml of water. Evaporation of the organic layer gave 3.2 g of crude product. Fractionation yielded 0.4 g of a liquid, b.p. 132—135°/0.5 mmHg, which solidified on standing (m.p. 111—115°). On the basis of the PMR characteristics and the analysis data structure VI was assigned to this product. (Found: C, 41.3; H, 5.0. $C_{16}H_{24}Sn_2$ calcd.: C, 42.35; H, 5.33%.)

Another fraction (0.60 g), boiling at 102—116°/0.5 mmHg consisted (GLC) of roughly equal amounts of Me_6Sn_2 and two unknown products. The PMR data of the latter compounds, isolated by preparative GLC, are consistent with structures IV and V.

In a similar way compound VII was obtained from the reaction of Me_6Sn_2 with *ortho*-diethynylbenzene.

Acknowledgements

The authors thank Dr. J.G. Noltes for critical discussions. Financial support by the International Tin Research Council, London, is gratefully acknowledged and we are indebted to Dr. W.E. Hoare for permission to publish the results.

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