Pergamon

Tetrahedron, Vol. 53, No. 4, pp. 1301-1310, 1997
Copyright © 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)01078-2

An Improved Synthesis of a Polymer-supported Distannane and its Application to Radical Formation

Jörg Junggebauer*[1] and Wilhelm P. Neumann†

Department of Chemistry, University of Dortmund, Otto-Hahn-Str. 6,
D-44227 Dortmund, Germany

Abstract: A polymer-supported distannane **1** was prepared by treatment of tin halide resin with lithium naphthalenide or sodium naphthalenide in THF. The content of the polymers **1** was determined to be 0.95 to 1.13 mmol/g tin as ditin. The polymer-supported distannane reagent was successfully applied to radical cyclizations of acyclic α-haloesters to yield γ-butyrolactones.

INTRODUCTION

Organotin compounds are often used as radical generating reagents for free radical reactions,[2,3] the most frequently applied reagent being tri-n-butyltin hydride.[4] In recent years, distannane reagents have gained an ample scope of synthetic applications,[3] since the use of tri-n-butyltin hydride is significantly limited by its excellent H-donor abilities.

In such radical syntheses, distannane reagents are often superior and convenient substitutes for tin hydrides, since the strength of the added H-donor can be adjusted to meet the thermodynamic and kinetic requirements of the radical reaction.[5-7]

Several different approaches[8] have been used to overcome the substantial drawback of product contamination by tin byproducts, but all of them failed to remove tin residues completely.

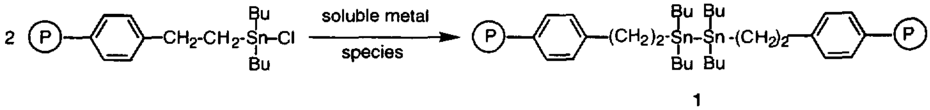
The substantial toxicity[9] of organotin compounds requires a different and more forward looking strategy. From an economic and ecological point of view, it is preferable to avoid product contamination instead of developing methods for the separation of tin byproducts. One such approach avoids product contamination by attaching the active tin species to inorganic[10] or organic polymeric matrices.[11]

We have recently published the preparation[5] and application[6,7] of a polymer-supported ditin reagent, while most of the synthetic interest has been focused on the development of polymer-supported tin hydrides.[11]

Now we present an improved synthesis of polymer-supported distannane providing higher yields and a significantly facilitated processing and workup procedure.

RESULTS AND DISCUSSION

A tin chloride resin was prepared following our usual synthesis[5] and subsequently converted into polymer-supported distannane **1** as outlined in Scheme 1.



1

Scheme 1. Preparation of polymer-supported distannane

The reductive coupling of two tin halide groups within a polymer matrix requires a soluble and active metal species. In our initial studies[5] on the preparation of polymer-supported distannane reagents, Bogdanovic magnesium[12] appeared to be the best suited reducing agent.

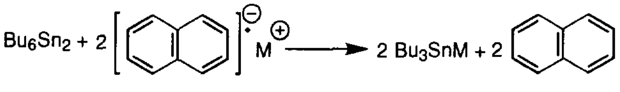
A significant problem became apparent when the distribution of the unchanged 0.3 mmol/g Sn-X groups inside the polymer beads was checked by means of electron microscopy and the EDAX (energy dispersive analysis of x-rays) method. While the tin and chlorine linescans of the tin chloride resin exhibited a homogeneous distribution over the whole diameter of a halved polymer bead before modification, the Sn-Cl groups, after treatment with magnesium-anthracene • 3 THF, were mainly located at the center of the resin. Apparently, the large magnesium-bearing anthracene system was not able to reach the inner sections of the resin and therefore the conversion of Sn-X functionalities into ditin was incomplete. In addition, the handling of the magnesium-anthracene • 3 THF requires very carefully adjusted reaction conditions, since the solubility as well as the formation of the active magnesium-anthracene • 3 THF, are extremely temperature dependent.[12] Extended reaction time under reflux conditions (4 days) was required to furnish a distannane resin in good yield (1.3 mmol/g tin as ditin, 81% conversion),[5] but approximately 20% Sn-Cl groups remained unreacted. Finally, the low solubility of anthracene in most organic solvents makes the separation of this compound from the distannane resin more difficult.

Since attempts to optimize the distannane synthesis with magnesium-anthracene • 3 THF[13] failed, a more reactive and at the same time more soluble reagent was sought. It is well known that lithium[14] and sodium[15] are capable of forming Sn-Sn bonds from triorganotin halides, but they also cleave these bonds when distannanes are treated with an excess of alkali metals[14b, 15c] or with sodium naphthalenide.[16] For both cases the formation of an intermediate trialkyltin alkali metal compound[14b, 15c] is proposed, as evidenced by trapping with alkyl halides (R'X).

$$\begin{array}{l} R_3SnX \xrightarrow{+\,2\,M} R_3SnM + MX \xrightarrow{+\,R_3SnX} R_6Sn_2 \\ R_3SnSnR_3 \xrightarrow{+\,2\,M} 2\,R_3SnM \xrightarrow{+\,2\,R'X} 2\,R_3SnR' + 2\,MX \end{array} \qquad \text{(eq. 1)}$$

Lithium naphthalenide or sodium naphthalenide[17] are potent reducing reagents and their excellent solubility in THF is essential for applications to polymeric matrices. Prior to any application of these metal species to preparation of polymeric ditin compounds it was important to investigate the extent of cleavage of the ditin bond upon exposure to alkali metal naphthalenides. To facilitate analysis, these experiments were run with hexabutylditin instead of **1**. The results were monitored by GC (with an internal standard) and by ^{119}Sn NMR.

Table 1. Formation of hexabutyl distannane employing alkali metal naphthalenides



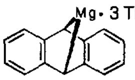
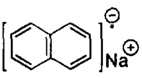
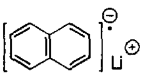
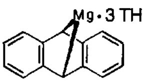
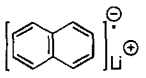
quenching:			Bu_6Sn_2	Bu_4Sn
excess butyl bromide:	entry 1	M = Li	98%	2%
	entry 2	M = Na	49%	51%

			Bu_6Sn_2	Bu_3SnH
excess isopropanol:	entry 3	M = Li	100%	-
	entry 4	M = Na	100%	-

Treatment of Bu_6Sn_2 with 2 equiv of lithium naphthalenide (Table 1, entry 1) and subsequent quenching with 1-bromobutane furnished only traces of Bu_4Sn (2%) as a quenching product of Bu_3SnLi, whereas the same experiment run with sodium naphthalenide yielded 51% Bu_4Sn as well as 49% hexabutyldistannane (entry 2).[18]

In our investigations, dry isopropanol turned out to be best suited for a workup of the reaction mixture, since no product other than hexabutyl ditin could be detected (entry 3 and 4). While for instance quenching with H_2O provided a significant amount of tin hydride, isopropanol exhibited the valuable capability of converting Bu_3SnLi or Bu_3SnNa into distannanes.[19] In addition, alkali metal salts are readily dissolved in isopropanol. When sodium naphthalenide and lithium naphthalenide were applied to the preparation of ditin functions on two different macroporous polystyrene polymers (BAYER R 984/90^R and R 985/90^R), the following results were obtained.

Table 2. Formation of polymer-supported distannane employing different soluble metal species

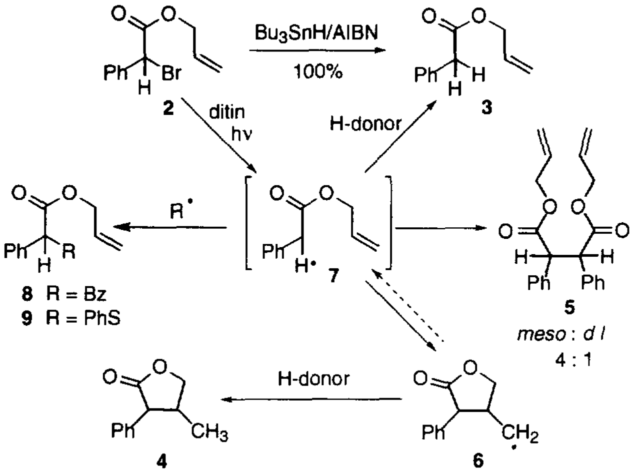
resin type / conditions	R 984/90^R			R 985/90^R	
	entry 1[5]	entry 2	entry 3	entry 4	entry 5[a]
reagent					
Sn-X content [mmol/g]	1.60 Sn-Cl	1.16 Sn-Cl	1.16 Sn-Cl	1.16 Sn-Cl	0.97 Sn-Cl 0.10 Sn-I 0.09 Sn-Br
reaction temp.	66°C	25°C	25°C	66°C	25°C
t [h]	96	12	12	96	12
Sn-X [mmol/g] unreacted	0.30 Sn-Cl	0.22 Sn-Cl	0.24 Sn-Cl	0.37 Sn-Cl	0.08 Sn-Cl
mmol Sn/g as Sn-Sn	1.30	0.96	0.95	0.84	1.13
conversion %	81%	83%	82%	72%	97%

a) polymer-supported distannane was several times recycled after use in radical reactions

A direct comparison of the data obtained with magnesium-anthracene • 3 THF (Table 2, entry 1 and 4) shows the impressive improvements gained by using alkali metal naphthalenide reagents. The reaction time could be shortened (from 96 h to 12 h) and the temperature was significantly lowered. By diminishing the percentage of unreacted Sn-X groups (entry 4 and 5), the degree of functionalization was substantially raised. An IR absorption of tin hydride (R_3Sn-H) at 1805 cm^{-1} could not be observed in any of these reactions.

To prove the value of polymer-supported distannane for organic synthesis, this reagent was used as a source of stannyl radicals in several radical cyclization reactions.

The radical reaction of α-bromo phenylacetic acid ester **2** with Bu_3SnH/AIBN under common radical reaction conditions (benzene, 80°C) as well as an application of the syringe technique (addition time 4 h, Table 3, entry 1) just yielded the undesired reduction product **3**.



Scheme 2. Product distribution in the radical reaction of **2**

When **2** was treated with polymer supported ditin **1**, three reaction products were observed depending on the strength of the H-donor applied. Table 3 shows the results of these reactions under variation of the ditin reagent and the H-donor.

Table 3. Results of the cyclization reactions of **2** employing different stannyl radical sources

entry	reagent	H-donor	T[°C]	t[h]	**4**	**5**	**3**	**8/9**
1	Bu_3SnH	benzene	80	5 h[a)]	-	-	100%	-
2	Bu_6Sn_2	isopropanol	55	23 h[c)]	39%	51%	8%	-
3		benzene	40	16 h[b)]	-	95%	5%	-
4	poly.-supp.	isopropanol	40	24 h[b)]	25%	72%	3%	-
5	distannane	benzene	75	24 h[c)]	-	96%	2%	-
6		toluene	40	26 h[b)]	22%	35%	4%	39% **8**[d)]
7		thiophenol	75	12 h[c)]	-	10%	55%	35% **9**[d)]

a) AIBN as radical initiator; b) rayonet reactor RPR 100 equipped with RPR 3000 tubes; c) daylight lamp Philips HPL-N 125 W; d) the structure of these byproducts was assigned by means of GC-MS and GC-FTIR (see Experimental Section)

Mild UV irradiation using moderate H-donors like isopropanol or toluene yielded the cyclic γ-butyrolactone **4** as the product of intramolecular radical attack to the allylic double bond and the dimerization product **5**. Using the week H-donor benzene as a solvent a mixture of *meso*- and *dl*-isomer (4 : 1) of the succinic acid derivative **5** was isolated in 95% yield. The separation of the pure reaction product without detectable tin contamination (^1H NMR) was achieved by simple filtration of the reaction mixture and evaporation of the solvent.

Apparently, we reached our goal to run radical reactions without any interference by strong H-donors. The application of well adjusted H-donors allows us to direct the reaction to the desired products, i. e. cyclization product **4** or dimer **5**.

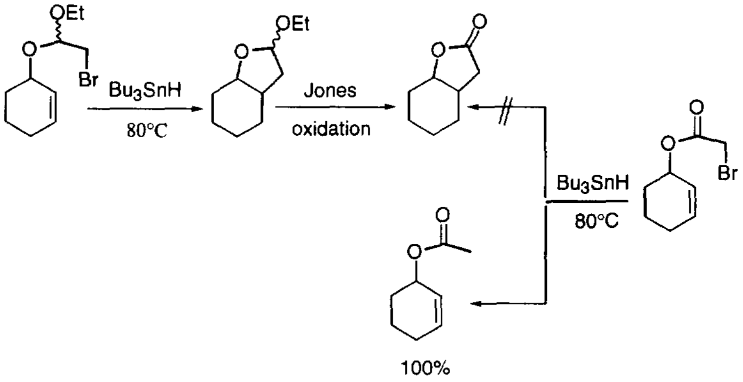
A reversibility of the intramolecular radical addition to the double bond must be proposed to explain the observed product distributions in different solvents. The cyclic primary methyl radical **6**, formed by addition to the CC-double bond, lacks any stabilization.

Two different fates of this radical are conceivable. Either it abstracts a proton from a H-donor to form the reduction product **3** or it undergoes ring opening to recover the thermodynamically favored, highly stabilized benzyl radical **7**. If the H-donor has a moderate strength, like isopropanol or toluene, the cyclic primary radical **6** is trapped to form **4**, whereas with weak H-donors like benzene no hydrogen can be transferred and the formation of the dimer **5** is strongly favored. The benzyl radical has just the single option to recombine since a disproportionation is impossible. This analysis is supported by investigations of Walling[20] who observed a reversibility of the cyclization reaction of the structually related 6-bromo-6-phenyl-1-hexene.

The long-lived benzyl radical **7** is subject to trapping reactions of radicals formed by hydrogen abstraction from the H-donors, i. e. toluene and thiophenol (Table 3, entries 6 and 7). Since the benzyl- (entry 6) and the phenylthiyl-radical (entry 7) are only present in very low concentrations in the reaction mixture, a recombination is unlikely. We therefore assume that the high yields of these recombination products (35% and 39%) are due to diffusion controlled processes inside the polymer beads.[21] These diffusion processes are subject to investigation in several groups and are still not very well understood.

Several attempts to prepare γ-butyrolactones by treatment of acyclic α-haloesters with Bu_3SnH have failed.[22,23] Since tin hydrides reduce the intermediate radicals in slow ester cyclizations even under dilute reaction conditions, the only isolated compound is often the product of simple reduction.

Therefore, Stork[22,24] and Ueno[23] independently developed a new route for the preparation of γ-butyrolactones starting from the corresponding α-bromo acetals. After completion of the radical cyclization step the cyclic acetal is converted into the desired γ-butyrolactone by Jones oxidation.

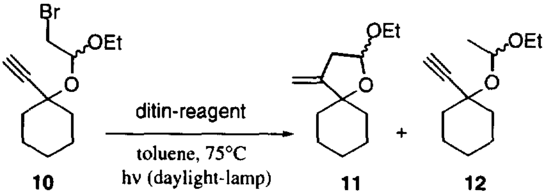


Scheme 3. Synthetic pathways to γ-butyrolactones

The success of this synthetic strategy is based on the significantly higher cyclization rates of acetals in comparison to esters.[24,25] In recent years this reaction sequence has often been employed for the preparation of naturally occurring compounds with lactone function, which supposedly possess tumor-inhibitor activity.

Ueno[26] applied this sequence of radical cyclization and subsequent oxidation to the preparation of the corresponding γ-butyrolactone in an overall yield of 39%. The primary radical cyclization step yielded only 63% of spiroketal **11**. The following table contains the yields and important experimental data of the radical reactions performed with Bu_6Sn_2 or polymer-supported distannane reagent.

Table 4. Results of the cyclization reaction of **10**

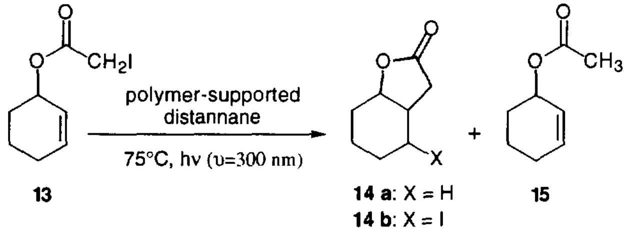


reagent	t [h]	**10**	**11**	**12**
Bu_3SnH26)	5-7 h	-	63%	-
Bu_6Sn_2	5 h	-	98%	-
polym.-supp. distannane	7.5 h	29%	68%	-

The use of Bu_6Sn_2 (0.5 equiv) as a source of stannyl radicals provided a clean reaction which yielded the cyclic acetal **11** as the only product. So does the reaction performed with polymer-supported ditin, but an amount of 29% of the starting material remained unreacted after 7.5 h. We assume that the decreased reactivity of the reagent **1** is due to the fact that the radical reaction strongly depends on the diffusion of the starting material **10** and the sensitizer to the reactive sites inside the polymer beads. Therefore the rate of the radical reaction slows down as soon as the ditin functions near the surface have reacted.

The superior properties of the Bu_6Sn_2/sensitizer/H-donor system allowed us to synthesize γ-butyrolactones from α-iodo esters.

Table 5. First application of polymer-supported distannane in the preparation of hexahydro benzo-2(3H)-furanone derivatives



distannane reagent	H-donor	**14 a**	**14 b**	**15**
0.5 equiv	toluene	35%	-	61%
0.1 equiv	benzene	5%	36%	50%

Upon treatment of **13** with 0.5 equiv distannane polymer 35% of γ-butyrolactone **14a** was formed. In this reaction the originally generated radical or the cyclized radical intermediate is trapped by an H-donor. When **13** was reacted with just 0.1 equiv of distannane reagent **1**, using Curran's iodo atom transfer method,[8a] 36% of the corresponding 4-iodo lactone **14b** as well as 5% of **14a** were isolated. The radical formed upon addition to the CC-double bond abstracts an iodine atom of the starting material to generate a new radical and to propagate the radical chain reaction.

To our knowledge, this is the first application of polymer-supported tin reagents to this synthetically valuable method.

The starting material for the functionalization with lithium naphthalenide (Table 2, entry 5) was used several times as a ditin resin in photochemically induced radical reactions and was recovered and regenerated to ditin polymer without loss of activity. The reaction mixture was simply filtered through a funnel with a fritted disc and the product could be easily isolated from the filtrate. The polymer was washed with organic solvents, i.e. diethyl ether or dichloromethane to remove traces of products and then it was regenerated for multiple use.

To establish the synthetic use of this polymer-supported distannane reagent the level of tin contamination of the cyclization products was evaluated by AAS measurements. Depending on the temperature and the irradiation period with UV-light the following tin contents of the reaction mixture were obtained.

Rayonet reactor (300 nm, 40°C, 35 h irradiation):	150 - 375 ppm
Daylight lamp (80°C, 31 h irradiation):	< 1100 ppm

Detailed studies reveal that the tin contamination is to a large extent due to abrasion of the polymeric matrix by the magnetic stirring bar and to a minor extent due to C-Sn-bond cleavage upon extended UV-irradiation. A simple filteration through a micro filter or even better, the use of of a shaker instead of a magnetical stirrer proved to reduce the level of tin contaminations significantly.[27]

Even though the determined level of tin contaminations is still to high for some applications with high purity standards, it is remarkably low in comparison to common photochemical reactions using Bu_6Sn_2 or Me_6Sn_2. Employing common photochemical reaction conditions with tin organic reagents a contamination of about 2 mol% even after chromatographic work-up is realistic.[8a] A synthesis applying polymer-supported ditin reagents provides without any troublesome workup a product almost free of tin byproducts (0.02 to 0.1 mol%).

CONCLUSION

This improved synthesis of polymer-supported ditin reagent provides an efficient and versatile radical source for organic synthesis. Besides multiple use, the most decisive advantage of polymer supported ditin reagents is the simple workup and the low level of tin contamination of the products. In combination with a suitable triplet sensitizer, this reagent is an alternative to tin hydride reagents.

EXPERIMENTAL SECTION

^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 NMR spectrometer employing $CDCl_3$ as a solvent and chloroform as the internal standard. Mass spectra were obtained on a Finnigan MAT 8230 and on a Finnigan MAT ITD 800 connected with a Dani 8521A. GC-FTIR spectra were recorded on a Bruker IFS 113 V and IFS 48. The AAS measurement were performed on a Perkin Elmer 1100 B. The gaschromatograms were recorded on a Carlo Erba HRGC 4160 equipped with a 25m CP-Sil 5 CB (1.3 µm) column and a Fisons Instruments GC-1900 (15 m DB-1701 (19)(1.0 µm).

Toluene, benzene, isopropanol and thiophenol were purified and dried according to common laboratory procedures.[28] Bu_6Sn_2 was prepared from Bu_3SnH with $Pd(PPh_3)_4$ as a catalyst.[29] α-Bromo phenylacetic acid allyl ester was prepared from α-bromo acetylbromide and allyl alcohol in presence of pyridine.[30] Commercially available 1-ethynyl cyclohexanol was treated with *N*-bromosuccinimide and ethyl vinyl ether to yield 1-(2-bromo-1-ethoxy-ethoxy)-1-ethylnyl-cyclohexane.[31] Cyclohex-2-en-1-ol was prepared from cyclohexene and NBS[30b] and subsequent reaction with sodium bicarbonate.[32] α-Bromo acetic acid cyclohex-2-enyl ester was prepared from cyclohex-2-en-1-ol and α-bromo acetyl bromide in pyridine.[30]

The reactions were monitored by GC employing the method of internal standard (nonane, dodecane) and by spectroscopic means as GC-FTIR and GC-MS. The products were identified by comparison with independently prepared authentic samples or by comparison with reported spectroscopical data of known compounds.

Procedure for the formation of polymer-supported distannane reagent

In a 250 ml 2-neck-flask fitted with a reflux condenser naphthalene was dissolved in dry THF (100 ml) under argon. Small portions of lithium (1 equiv) were added and after completion of the addition the deep green solution was stirred for 2 h at RT. The concentration of this solution was determined by acidimetric titration.[33] An equimolar amount of this lithium naphthalenide solution was added to a flask in which 20 g of Sn-Cl-resin of known content of Sn-Cl groups was shaken in 250 ml of dry THF with the help of a shaker. After 12 h of shaking, the green colour had disappeared and the reaction mixture was quenched with isopropanol. The resin was washed several times with isopropanol and diethylether and dried under high vacuum. Analysis of polymer-supported distannane reagents[11a]: Sn: gravimetry; Sn-Sn and Sn-I: iodometry, Sn-Br and Sn-Cl: argentometry

General procedure for the reaction with distannane or polymer-supported distannane

The polymer-supported distannane reagent (0.5 equiv) or Bu_6Sn_2 (0.5 equiv), sensitizer (6 equiv acetone or *p*-methoxyacetophenone) were added to a 0.1 M solution of radical precursor in an absolute and degassed solvent. The reaction mixture was further degassed by three freeze-pump-thaw cycles and then either irradiated by a daylight lamp (Philips HPL-N 125 W) in a heated water bath or in a rayonet reactor RPR 100 equipped with RPR 3000 tubes (υ=300 nm, Southern New England Ultraviolet Company, Hamden, CT/USA) at approximately 40°C. For experimental details see Schemes.

Bu_3SnH addition with syringe technique

A solution of Bu_3SnH (1.2 equiv) and AIBN in 20 ml of dry benzene was added by a syringe pump within 4 h to a 0.05 M solution of radical precursor in dry benzene at reflux temperature. After completion of the reaction the solvent was evaporated and the product purified by chromatographic work-up (silica gel, hexane : ethyl acetate 19 : 1).

2,3-diphenyl succinic acid diallyl ester (**5**)[34]. The *meso* : *dl* ratio was determined by ^{1}H NMR integration to 4 : 1. *meso*-configuration **5** : ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.21-4.36 (m, 4 H, ^3J = 13.4 Hz, 5.5 Hz, ^2J = 1.3 Hz), 4.47 (s, 2 H), 4.95 (dd, 2 H, ^3J = 17.1 Hz, ^2J = 1.3 Hz), 5.04 (dd, 2 H, ^3J = 10.5 Hz, ^2J = 1.3 Hz), 5.52-5.65 (m, 2 H) 7.00-7.51 (m, 10 H); *dl*-configuration **5** : ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 4.33 (s, 2 H), 4.54-4.72 (m, 4 H), 5.19 (dd, 2 H, ^3J = 10.5 Hz, ^2J = 1.3 Hz), 5.23 (dd, 2 H, ^3J = 17.1 Hz, ^2J = 1.3 Hz), 5.83-5.94 (m, 2 H), 7.00-7.51 (m, 10 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ = 54.85 (d, *dl*) 55.19 (d, *meso*), 65.35 (t, *meso*), 65.67 (t, *dl*), 117.79 (t, *meso*), 118.02 (t, *dl*), 127.43, 127.96, 128.04, 128.39, 128.44, 128.54, 128.68, 128.78, 131.56 (d, *meso*), 131,84 (d, *dl*), 135.59 (s, *dl*), 136.23 (s, *meso*), 171.00 (s, *meso* + *dl*); IR (KBr) 1723 (vs, C=O), 1651 (w, C=C), 1291 (s, C-O), 1151 cm^{-1}(s, C-O); MS (70 eV): m/z = 350 (12%, M^+), 292 (100%, M^+- C_3H_5OH), 264 (60%, M^+- C(O)-OC_3H_5), 251 (13%), 180 (81%, M^+- 2 C(O)-OC_3H_5), 175 (10%, PhCH-C(O)-OC_3H_5), 165 (35%), 147 (38%, PhCH-OC_3H_5), 118 (20%, PhCH=C=O), 105 (31%, $C_7H_9^+$), 91 (83%, $C_7H_7^+$), 77 (13%, $C_6H_5^+$)

2,3-Diphenyl propionic acid allyl ester (**8**). GC-MS: m/z = 266 (10%, M^+), 221 (50%, M^+ - C_2H_5O), 181 (46%, M^+ - C(O)-OC_3H_5), 165 (35%), 147 (38%, M^+ - PhCH-OC_3H_5), 118 (15%, PhCH=C=O), 103 (30%), 91 (45%, $C_7H_7^+$), 77 (16%, $C_6H_5^+$); GC-FTIR: 1751 (vs, C=O), 1645 (w, C=C), 1248 (s, C-O), 1151 cm^{-1} (s, C-O)

Phenyl-phenylsulfanyl-acetic acid allyl ester (**9**). GC-MS: m/z = 284 (50%, M^+), 239 (7%, M^+ - C_2H_5O), 199 (100%, M^+ - C(O)-OC_3H_5), 165 (12%), 121 (10%, Ph-CH-S^+), 109 (30%, Ph-S^+), 91 (33%, $C_7H_7^+$), 77 (7%, $C_6H_5^+$); GC-FTIR: 1751 (vs, C=O), 1645 (w, C=C), 1248 (s, C-O), 1151 cm^{-1} (s, C-O)

AAS experiments

The samples for the AAS experiments were prepared following the general procedure for the radical reactions with polymer-supported distannane. We chose toluene as the solvent and as the sensitizer we used acetone for the reaction at 40°C (35 h, 300 nm) and p-methoxyacetophenone for the reaction at 80°C (31 h, daylight lamp). Hexabutyl distannane was employed for the standard solutions due to its chemical similarity with polymer-supported distannane and its good AAS properties. [35]

ACKNOWLEDGEMENTS

We would like to thank T. Niebuhr for performing the AAS measurements. This work has been supported by the Volkswagen Stiftung and the Fonds der Chemischen Industrie. We are grateful to BAYER AG, Leverkusen for the kind supply of polystyrene starting material.

REFERENCES AND NOTES

† deceased in August 1993

1. present address: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA
2. a) Neumann, W. P. *Die Organische Chemie des Zinns*, Ferdinand Enke: Stuttgart, **1967**; *The Organic Chemistry of Tin:*, John Wiley: London, **1970**; b) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*, Butterworths: London, **1987**; c) Yamamoto, Y. (ed.) *Organotin compounds in Organic Synthesis, Tetrahedron Symposium-in-print* No. 36, Pergamon Press: London, **1989**, *45*, 909-1229
3. a) Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*, VCH: Weinheim, **1995**; b) Curran, D. P. *Synthesis* **1988**, 417-488; 489-513; c) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon bonds*, Pergamon Press: Oxford, **1986**, d) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237-1286
4. Neumann, W. P. *Synthesis* **1987**, 665-683
5. Harendza, M.; Leβmann, K.; Neumann, W. P. *Synlett* **1993**, 283-285
6. Harendza, M.; Junggebauer, J; Leβmann, K.; Neumann, W. P. Tews, H.; *Synlett* **1993**, 286-288
7. Harendza, M.; Junggebauer, J.; Leβmann, K.; Neumann, W. P. Tews, H.; *Proc. Indian Acad. Sci.-Chem. Sci.* **1993**, *105*, 5915-5925
8. a) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140-3157; b) Berge, J. M.; Roberts, S. M. *Synthesis* **1979**, 471-472; c) Barton, D. H. R.; Hay Motherwell, R. S.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. I* **1981**, 2363-2367
9. a) Wirth, W.; Gloxhuber, C. *Toxikologie*, 5. Ed.; Thieme: Stuttgart, **1994**; b) Smith, P. J. *Toxicological Data on Organotin Compounds*; Publication 538, International Tin Research Institute, London, **1978**
10. Schumann, H.; Pachaly, B. *J. Organomet. Chem.* **1982**, *233*, 281-289
11. Polymeric tin reagents: a) Gerigk, U.; Gerlach, M.; Neumann, W. P.; Vieler, R.; Weintritt, V. *Synthesis* **1990**, 448-452; b) Peterseim, M.; Neumann, W. P. *Reactive Polymers* **1993**, *20*, 189; c) Dumartin, G.; Ruel, G.; Kharboutli, J.; Delmond, B.; Connil, M.-F.; Jousseaume, B.; Pereyre, M. *Synlett* **1994**, 952-954. Perfluorinated tin hydride: d) Curran, D. P.; Hadida, S. *J. Am. Chem. Soc.* **1996**,*118*, 2531-2532. Water soluble tin hydrides: e) Light, J; Breslow, R. *Tetrahedron Lett.* **1990**, *31*, 2957-2958; f) Rai, R.; Collum, D. B. *Tetrahedron Lett.* **1994**, *35*, 6221-6224. Acid soluble tin hydrides: g) Clive, D. L. J.; Yang, W. *J. Org. Chem.* **1995**, *60*, 2607-2609; h) Vedejs, E.; Duncan, S. M.; Haight, A. R. *J. Org. Chem.* **1993**, *58*, 3046-3050
12. Bogdanovic, B.; Liao, S.; Mynott, R.; Schlichte, K.; Westeppe, U. *Chem. Ber.* **1984**, *117*, 1378-1392
13. Catalytic quantities of anthracene as a carrier for magnesium were successfully applied in syntheses: Bogdanovic, B. personal communication, Mülheim/Ruhr, 1993; Attempts to apply anthracene in catalytical amounts (0.5 eq. referring to magnesium) to distannane formation failed. Even after 150 h a content of only 0.55 mmol/g tin as ditin was obtained.
14. a) Wittig, G.; Meyer, F. J.; Lange, G. *Liebigs Ann. Chem.* **1951**, *571*, 167-201; b) Gilman, H.; Marrs, O. L.; Sim, S.-Y. *J. Org. Chem.* **1962**, *27*, 4232-4236

15. a) Krause, E.; von Grosse, A. *Die Chemie der Metall-organischen Verbindungen*, Saendig: Wiesbaden, **1965**; b) Brown, M. P., Fowles, G. W. A. *J. Chem. Soc.* **1958**, 2811-2814; c) Quintard, J. P.; Pereyre, M. in: Gielen, M. (ed.) *Rev. Silicon, Germanium, Tin and Lead compounds* **1984**, *4*, 154
16. a) Kühlein, K; Neumann, W. P.; Mohring, H. *Angew. Chem.* **1968**, *80*, 438-439; *Angew. Chem., Int. Ed. Engl.* **1968**, *80*, 455-456; b) Kuivila, H. G.; Considine, J. L.; Kennedy, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 7206-7208; c) Blake, D.; Coates, G. E.; Tate, J. M. *J. Chem. Soc.* **1961**, 618-622; d) Wursthorn, K. R.; Kuivila, H. G.; Smith, G. F. *J. Am. Chem. Soc.* **1978**, *100*, 2779-2788
17. Ebel, H. F.; in: *Houben-Weyl*, 4th Ed., Mueller, E. (ed.) Thieme: Stuttgart **1970**, Vol.*13/1*, 378-383
18. A severely lowered reactivity of lithium in comparison to sodium towards distannanes has been reported: Ingham, R. K.; Gilman, H.; in: Stone, F. G. A.; Graham, W. A. G. (eds.) *Inorganic Polymers: Organopolymers of Group IV Elements*, Academic Press: New York **1962**, 321
19. Similar results were observed upon quenching with CO_2[14].
20. Walling, C., Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6064-6069
21. None of these recombination products could be observed in significant yields in reactions with monomeric hexabutyl ditin.
22. Stork, G.; Mook, R.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741-3742
23. Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564-5566
24. Stork, G.; in: Nozaki, H. (ed.) *Current Trends in Organic Chemistry*, Pergamon Press: Oxford, **1983**, 359
25. Beckwith, A. L. J.; Ingold, K. U.; in: de Mayo, P. (ed.) *Rearrangements in Excited States*, Academic Press: New York, **1980**, 162
26. Moriya, O.; Okawara, M.; Ueno, Y. *Chem. Lett.* **1984**, 1437-1440
27. a) Leβmann, K. *Ph. D. thesis*, University of Dortmund **1992**; b) Harendza, M. *Ph. D. thesis*, University of Dortmund **1993**
28. Perrin, D. D.; Amarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; 2nd Ed., Pergamon Press: Oxford, **1980**
29. Bumagin, N.; Gulevich, Y. V.; Beletskaya, I. P. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1984**, 1137; *Bull. Acad. Sci. USSR, Chem. Ser.* **1984**, *33*, 1044
30. a) Tietze, L. F.; Eicher, Th. *Reaktionen und Synthesen im organisch-chemischen Praktikum*, Thieme, Stuttgart, **1981**; b) Autorenkollektiv, *Organikum: Organisch-chemisches Grundpraktikum*, 15. Ed.; VEB Dt. Verlag der Wissenschaften: Berlin, **1981**
31. Mantione, R. *Bull. Soc. Chim. Fr.* **1969**, 4523-4527
32. Geibel, K.; Hofmann, H.; Kropf, H.; Thiem, J. in: *Houben-Weyl*, 4th Ed., Kropf, H. (ed.), Thieme: Stuttgart **1979**, Vol. *6/1a*, 189
33. Gilman, H.; Zoellner, E. A.; Dickey, J. B. *J. Am. Chem. Soc.* **1929**, *51*, 1576-1583
34. The configuration was assigned in analogy to reported ^{1}H NMR spectra of succinic acid derivatives: Larsson, E.; Org. Magn. Reson. **1974**, *6*, 103-105
35. Niebuhr, T. *Diploma thesis*, University of Dortmund **1994**

(*Received in Germany* 5 *September* 1996; *accepted* 18 *November* 1996)