Journal of Organometallic Chemistry, 365 (1989) C1–C5
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09563PC

Preliminary communication

Novel asymmetric triorganotin hydrides containing the (–)-menthyl ligand *

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(Received July 25th, 1988)

Abstract

Synthesis and characterization of (–)-menthylmethyl-t-butyltin hydride and (–)-menthylmethylisopropyltin hydride, asymmetric triorganotin hydrides with the chiral tin center linked to a chiral carbon of an optically active substituent, and of (–)-menthyldimethyltin hydride are reported.

Triorganotin hydrides have proved to be of high synthetic utility [1]. One field of application is the selective reduction of haloalkanes [2]. In order to utilize organotin hydrides as asymmetric reducing agents in the synthesis of optically active alkanes, asymmetric organotin hydrides having an optically active (–)-menthoxy or (–)-bornoxy group bound to the chiral tin center had been synthesized [3]. In this case, the optically active substituent induces asymmetry during the free radical chain process of organotin hydride reduction of haloalkanes [4]. Under such conditions asymmetric triorganotin hydrides with the tin atom being the only chiral center lose their optical activity [5].

We have now synthesized the first asymmetric triorganotin hydrides with an optically active substituent, a (–)-menthyl group, bound directly to tin by a chiral carbon. In contrast to the asymmetric tin hydrides having the optically active group bound via oxygen, these new compounds not only have the advantage of being quite more stable but also should show a more effective asymmetric induction (1,2-induction as opposed to 1,3-induction).

Starting from optically active (–)-menthyl chloride ($[\alpha]_D^{20}$ –44.6° (neat)) [6], the corresponding Grignard reagent [7] reacts with trimethyltin chloride to give solely (–)-menthyltrimethyltin (**1**). No (+)-neomenthyltrimethyltin is formed. Subsequent monobromodemetallation [8] yields (–)-menthyldimethyltin bromide (**2**), which

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* In memoriam Professor Dr. Jerold J. Zuckerman.

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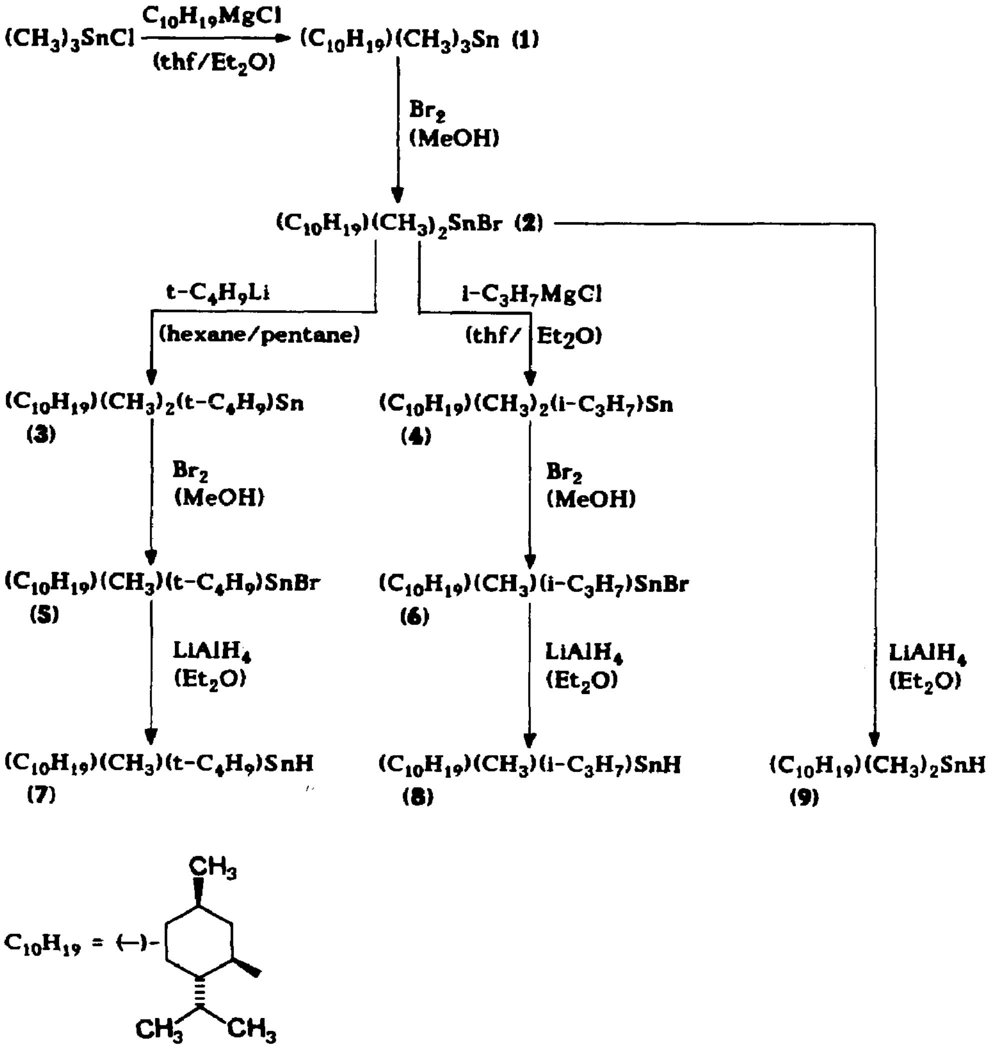

Scheme 1

after treatment with t-butyllithium or isopropylmagnesium chloride affords (−)-menthyldimethyl-t-butyltin (**3**) or (−)-menthyldimethylisopropyltin (**4**), respectively. A second selective monobromination leads to (−)-menthylmethyl-t-butyltin bromide (**5**) or (−)-menthylmethylisopropyltin bromide (**6**), both having an asymmetric tin center. The corresponding asymmetric triorganotin hydrides, (−)-menthylmethyl-t-butyltin hydride (**7**) and (−)-menthylmethylisopropyltin hydride (**8**), are obtained by the reduction with lithium aluminum hydride. In addition, (−)-menthyldimethyltin hydride (**9**) was synthesized by the direct reduction of the prochiral (−)-menthyldimethyltin bromide (**2**) (Scheme 1).

The hydrides **7**, **8** and **9** could be isolated in an overall yield of 42, 55, or 78% (relative to starting trimethyltin chloride), respectively. The colorless, distillable liquids decompose slowly on exposure to air as detected by the decrease of the ν(Sn–H) (within 17 days, the band intensity reduces to 20%). However, when stored under an inert atmosphere at −20 °C, the hydrides show no decomposition.

Table 1

Selected NMR data for the (−)-menthyldiorganotin hydrides **7**, **8**, **9**

	^{1}H NMR [a,c]	
	H–Sn	CH_3–Sn
7	δ 5.25 ppm (m [g]) $^{1}J(^{1}H^{117/119}Sn)$ 1458.0/1526.4 Hz	δ 0.20 ppm (d; $^{3}J(^{1}HCSn^{1}H)$ 2.6 Hz) $^{2}J(^{1}HC^{117/119}Sn)$ 45.9/48.1 Hz δ′ 0.18 ppm (d; $^{3}J(^{1}HCSn^{1}H)$ 2.6 Hz) $^{2}J'(^{1}HC^{117/119}Sn)$ 45.7/47.8 Hz
8	δ 5.11 ppm (m [g]) $^{1}J(^{1}H^{117/119}Sn)$ 1486.4/1555.5 Hz	δ 0.16 ppm (d; $^{3}J(^{1}HCSn^{1}H)$ 2.6 Hz) $^{2}J(^{1}HC^{117/119}Sn)$ 47.0/49.2 Hz δ′ 0.15 ppm (d; $^{3}J(^{1}HCSn^{1}H)$ 2.5 Hz) $^{2}J'(^{1}HC^{117/119}Sn)$ 46.9/49.0 Hz
9	δ 4.96 ppm (sep; $^{3}J(^{1}HSnC^{1}H)$ 2.5 Hz) $^{1}J(^{1}H^{117/119}Sn)$ 1570.9/1644.0 Hz	δ 0.19 ppm (d; $^{3}J(^{1}HCSn^{1}H)$ 2.5 Hz) $^{2}J(^{1}HC^{117/119}Sn)$ 50.4/52.7 Hz
	$^{13}C\{^{1}H\}$ NMR [b,c]	$^{117}Sn\{^{1}H\}$ NMR [d,e,f]
	CH_3–Sn	
7	δ −13.9 ppm $^{1}J(^{13}C^{117/119}Sn)$ 257.5/269.4 Hz δ′ −14.5 ppm $^{1}J'(^{13}C^{117/119}Sn)$ 255.9/268.0 Hz	δ −57.5 ppm (48) δ′ −62.2 ppm (52)
8	δ −14.8 ppm $^{1}J(^{13}C^{117/119}Sn)$ 269.0/281.6 Hz δ′ −15.1 ppm $^{1}J'(^{13}C^{117/119}Sn)$ 269.0/281.3 Hz	δ −68.8 ppm (51) δ′ −70.2 ppm (49)
9	δ −12.6 ppm $^{1}J(^{13}C^{117/119}Sn)$ 300.0/314.0 Hz δ′ −12.8 ppm $^{1}J'(^{13}C^{117/119}Sn)$ 300.1/314.0 Hz	δ −96.8 ppm

[a] 80 MHz (Bruker WP 80) in C_6D_6. [b] 20.15 MHz (Bruker WP 80 SY) ^{1}H broadband decoupled in C_6D_6. [c] Chemical shifts are referenced to $(CH_3)_4Si$ with positive shifts referring to lower field. [d] 28.552 MHz (Bruker WP 80 SY) ^{1}H inverse gated decoupled in C_6D_6. [e] Chemical shifts are referenced to $(CH_3)_4Sn$ with positive shifts referring to lower field. [f] Relative integral ratio in parentheses. [g] Only partially resolved.

Multinuclear NMR investigations not only fully characterize **7**, **8** and **9** but also demonstrate the existence of two diastereomers of **7** or **8**, respectively (Table 1). The ^{1}H and ^{13}C NMR spectra of **7** and **8**, in which the optically active ligand is attached to a chiral tin center, each show two distinct $CH_3(Sn)$ resonances due to two diastereomers. Furthermore, additional carbon atoms either adjacent or close to tin also give rise for two ^{13}C signals. **9**, prochiral at the tin center, shows two ^{13}C $CH_3(Sn)$ resonances, too. However, they are caused by the magnetic non-equivalence of the two diastereotopic methyl groups in the molecule. The ^{1}H NMR spectrum of **9** reveals no anisochronism of the respective methyl protons.

The diastereomers of **7** and **8** are not formed in an equal ratio as detected by means of ^{117}Sn NMR (NOE suppressing ^{1}H decoupling technique [9]), thus indicating the influence of the optically active substituent at tin.

Investigations of the applicability of these (−)-menthyldiorganotin hydrides to the enantioselective reduction of haloalkanes are in progress.

Experimental

All reactions were carried out under exclusion of oxygen and water in an atmosphere of argon using Schlenk tube technique. For carbon and hydrogen analyses a Perkin–Elmer 240 C elemental analyzer, for the determination of the tin content a Perkin–Elmer 2380 atomic absorption spectrophotometer were used. Infrared spectra were recorded on a Perkin–Elmer 457 grating infrared spectrophotometer. Optical rotations were measured on a Polartronic-D (Schmidt + Haensch) polarimeter using a 2 dm cell.

(−)-Menthyltrimethyltin (1). A solution of 75.1 g (377 mmol) trimethyltin chloride in 340 ml diethyl ether is added dropwise over a period of 5 h at 0 °C to a vigorously stirred solution of (−)-menthylmagnesium chloride prepared from 130 g (744 mmol) (−)-menthyl chloride and 23.2 g (955 mmol) magnesium in 475 ml tetrahydrofuran. After stirring for 48 h at room temperature, the mixture is treated dropwise with 7.4 ml (411 mmol) water at 0 °C, stirred for further 60 min at room temperature and dried over anhydrous Na_2SO_4. Removal of the solvents and destillation gives **1** as a colorless liquid. Yield: 107 g (94%), b.p. 75 °C/1.4 mbar. Found: C, 51.38; H, 9.38; Sn, 39.34. $C_{13}H_{28}Sn$ calcd.: C, 51.52; H, 9.31; Sn, 39.17%. $[\alpha]_D^{20}$ −32.5° (*c* 2.12; benzene).

(−)-Menthyldimethyltin bromide (2). To a vigorously stirred suspension of 100 g (330 mmol) **1** in 1200 ml methanol at 0 °C are added dropwise 51.7 g (324 mmol) bromine under exclusion of light. Stirring for 12 h at room temperature affords an orange solution. Removal of the methanol and distillation gives **2** as a colorless liquid. Yield: 114 g (96%), b.p. 86°/0.15 mbar. Found: C, 39.26; H, 6.75; Sn, 31.69. $C_{12}H_{25}BrSn$ calcd.: C, 39.17; H, 6.85; Sn, 32.26%. $[\alpha]_D^{20}$ −31.6° (*c* 1.45; benzene).

(−)-Menthyldimethyl-t-butyltin (3). To a stirred solution of 28.0 g (76.1 mmol) **2** in 200 ml pentane at 0 °C are slowly added 60.6 ml of an 1.7 *M* solution of t-butyllithium in pentane (103 mmol). The mixture is stirred for 12 h at room temperature, treated dropwise at 0 °C with 1.85 ml (103 mmol) water and stirred for 1 h again at room temperature. After drying over anhydrous Na_2SO_4, removal of the solvent and distillation, **3** is obtained as a colorless liquid. Yield: 18.9 g (72%), b.p. 72 °C/0.02 mbar. Found: C, 55.33; H, 9.99; Sn, 34.98. $C_{16}H_{34}Sn$ calcd.: C, 55.68; H, 9.93; Sn, 34.39%. $[\alpha]_D^{20}$ −30.5° (*c* 1.54; benzene).

(−)-Menthyldimethylisopropyltin (4). In analogy to the synthesis of **1**, the reaction between 26.0 g (70.7 mmol) **2** and isopropylmagnesium chloride made from 11.1 g (141 mmol) isopropyl chloride and 4.41 g (181 mmol) magnesium affords **4** as a colorless liquid. Yield: 20.6 g (88%), b.p. 63 °C/0.01 mbar. Found: C, 54.62; H, 9.73; Sn, 36.23. $C_{15}H_{32}Sn$ calcd.: C, 54.41; H, 9.74; Sn, 35.85%. $[\alpha]_D^{20}$ −30.7° (*c* 1.48; benzene).

(−)-Menthylmethyl-t-butyltin bromide (5). In analogy to the synthesis of **2**, 16.6 g (48.1 mmol) **3** and 7.54 g (47.2 mmol) bromine react during 48 h with formation of **5** as a colorless liquid. Yield: 16.5 g (85%), b.p. 95 °C/0.02 mbar. Found: C, 43.94; H, 7.47; Sn, 29.39. $C_{15}H_{31}BrSn$ calcd.: C, 43.94; H, 7.62; Sn, 28.95%. $[\alpha]_D^{20}$ −30.9° (*c* 1.83; benzene).

(−)-Menthylmethylisopropyltin bromide (6). In analogy to the synthesis of **2**, 18.4 g (55.6 mmol) **4** and 8.70 g (54.4 mmol) bromine react during 30 h to give **6** as a colorless liquid. Yield: 19.0 g (88%), b.p. 92 °C/0.02 mbar. Found: C, 42.19; H, 7.32; Sn, 30.31. $C_{14}H_{29}BrSn$ calcd.: C, 42.46; H, 7.38; Sn, 29.98%. $[\alpha]_D^{20}$ −29.5° (*c* 1.45; benzene).

(−)-Menthylmethyl-t-butyltin hydride (7). A solution of 14.8 g (36.1 mmol) **5** in 30 ml diethyl ether is slowly added to a stirred suspension of 1.37 g (36.1 mmol) $LiAlH_4$ in 60 ml diethyl ether at 0 °C. After stirring for 5 h at room temperature, 2.6 ml (144 mmol) water in 9.2 ml dioxane are added dropwise at 0 °C. The mixture is stirred for further 15 min at room temperature. Filtration and subsequent washing of the residue three times with 15 ml diethyl ether affords a colorless solution, which is dried over anhydrous Na_2SO_4. Removal of the solvent and distillation gives **7** as a colorless liquid. Yield: 9.1 g (76%), b.p. 62 °C/0.06 mbar. Found: C, 54.55; H, 9.52; Sn, 35.20. $C_{15}H_{32}Sn$ calcd.: C, 54.41; H, 9.74; Sn, 35.85%. ν(Sn–H) 1772 cm^{-1} (s; film). $[\alpha]_D^{20}$ $-31.6°$ (*c* 1.52; benzene).

(−)-Menthylmethylisopropyltin hydride (8). In analogy to the synthesis of **7**, 17.1 g (43.2 mmol) **6** and 1.64 g (43.2 mmol) $LiAlH_4$ react with formation of **8** as a colorless liquid. Yield: 10.8 g (79%), b.p. 72 °C/0.1 mbar. Found: C, 52.75; H, 9.63; Sn, 37.93. $C_{14}H_{30}Sn$ calcd.: C, 53.03; H, 9.54; Sn, 37.44%. ν(Sn–H) 1786 cm^{-1} (s; film). $[\alpha]_D^{20}$ $-29.8°$ (*c* 1.66; benzene).

(−)-Menthyldimethyltin hydride (9). In analogy to the synthesis of **7**, the reaction between 32.0 g (87.0 mmol) **2** and 3.30 g (87.0 mmol) $LiAlH_4$ affords **9** as a colorless liquid. Yield: 21.6 g (86%), b.p. 56 °C/0.07 mbar. Found: C, 49.66; H, 9.02; Sn, 41.65. $C_{12}H_{26}Sn$ calcd.: C, 49.86; H, 9.07; Sn, 41.07%. ν(Sn–H) 1798 cm^{-1} (s; film). $[\alpha]_D^{20}$ $-32.5°$ (*c* 1.87; benzene).

Acknowledgements. This work has been supported by the Fonds der Chemischen Industrie and by NATO as well as by special grants in connection with the exchange program Technische Universität Berlin/The University of Oklahoma.

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