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Synthesis and Some Reactions of the First Chiral Tin Hydride Containing a C_2-Symmetric Binaphthyl Substituent

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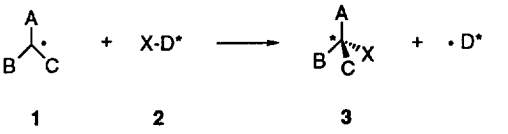
Abstract: Starting from pure (*S*)-2,2'-bis(bromomethyl)-1,1'-binaphthyl, the synthesis of a new chiral, enantiomerically pure dinaphthostannepin is described. Preliminary reactions of this hydride with a racemic organic halide under radical conditions gave the reduced product in up to 41% enantiomeric excess, depending on the experimental conditions.

During the last decade, radical reactions have become a very powerful tool for synthetic organic chemists and there are now many syntheses involving radical processes as key steps.[1] The importance of radical reactions has grown even more since the discovery that they can proceed with high stereoselectivity. Many examples have already been reported in which stereocontrol has been achieved through the use of chiral auxiliaries, either linked to the radical center or to the radical trap, or by 1,2-asymmetric induction.[2] The influence of Lewis acids on the diastereoselectivity of radical processes[3] has begun to be receive attention, and recently the first enantioselective reactions with chiral Lewis acids have been reported.[4]

In principle, stereocontrol can occur in an atom- or group-transfer reaction between a prostereogenic radical **1** and a chiral radical trap **2** (Scheme 1). This reaction, whose prototype is the reduction of a racemic organic halide with a chiral triorganotin hydride, can afford product **3** (X = H) as a non-racemic mixture through the intermediacy of diastereomeric transition states. Examples of such transformations are rare and this is one of the greatest challenges in the field of radical reactions.

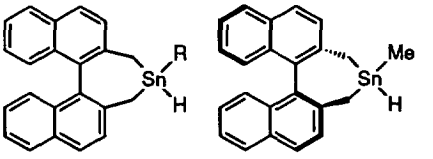


1 **2** **3**

Scheme 1

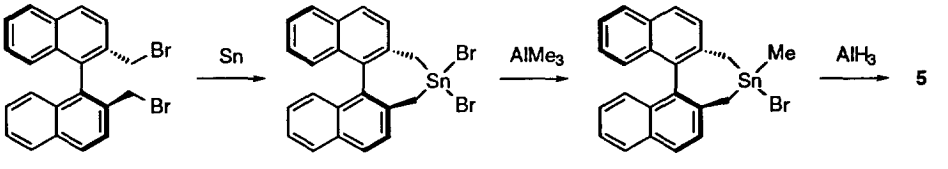
The few known chiral triorganotin hydrides have either a stereogenic tin atom[5] or a tin substituent bearing a stereogenic center.[6] Examples in which a chiral tin hydride is employed in enantioselective reactions include the reduction of chloroalkanes with diorgano(alkoxy)tin hydrides, giving the corresponding alkanes in up to 32% enantiomeric excess (ee),[6b] and the reduction of acetophenone with dineophyl(–)-menthyltin hydride, affording (*S*)-(–)-1-phenylethanol in 40% ee.[6f] The second reaction is different from the reaction depicted in Scheme 1 because its first step (the addition of a stannyl radical to the oxygen atom of the ketone) generates a prostereogenic radical bearing a chiral group. The subsequent hydrogen abstraction takes place in the presence of a chiral auxiliary on the radical center.

The axially-dissymmetric binaphthyl group has been extensively used as a chiral auxiliary for asymmetric synthesis,[7] and many methods have already been reported for the optical resolution of racemic derivatives[8] or direct enantioselective synthesis of optically active binaphthyls.[9] The improved access to pure (*R*)- and (*S*)-2,2'-dimethyl-1,1'-binaphthyl,[10] together with a few reported examples of compounds containing a stannepin ring fused with the binaphthyl moiety,[11] suggested the synthesis of tin hydrides of type **4** should be possible. Here we report the synthesis of the new chiral, enantiomerically pure tin hydride **5** and its preliminary reactions with a chiral organic halide.



4 **5**

Following the reported procedure,[10] pure (*S*)-2,2'-bis(bromomethyl)-1,1'-binaphthyl **6** was obtained in 5 steps from the commercially available 1-bromo-2-methylnaphthalene. Reaction of **6** with tin powder in refluxing toluene in the presence of trace amounts of water gave the dibromostannepin **7** (Scheme 2);[11c] this compound is completely insoluble in diethyl ether and can be recovered pure in 80-85% yield simply by washing with ether the product obtained after filtration of the reaction mixture and evaporation of the solvent.



6 **7** **8**

Scheme 2

The apparently straightforward conversion of **7** to **5** proved quite difficult.[12] Ultimately, monoalkylation of **7** was accomplished by treatment with trimethylaluminum (2.0 M solution in toluene, 1 equiv) in THF at 25 °C for 30 min. After workup with 4% HBr and extraction with ether, pure stannepin **8** was isolated in 85-90% yield; contamination from the dimethylated compound was lower than 1% (^{1}H-NMR analysis). Hydride **5** was eventually obtained by reduction of **8** with alane (1 equiv) in THF at 25 °C for 1 h. After quenching and extraction with ether, pure **5** was recovered in almost quantitative yield without any significant contamination. Compound **5** was fully characterized, and it is the first triorganotin hydride containing the C_2-symmetric binaphthyl moiety. The hydride partially decomposes if kept overnight at r.t. in benzene solution. As a solid, it can be stored at r.t. under an argon atmosphere for a few days, but after 2 weeks, a ^{1}H-NMR spectrum revealed the appearance of new broad peaks in the benzylic region. For this reason, all of the following reactions involving **5** were carried out with freshly prepared hydride.

The first chiral halide to be tested was racemic 2-bromo-1,2-diphenylpropan-1-one **9**, readily accessible through methylation[13a] and bromination[13b] of the commercially available deoxybenzoin: reduction of **9** with hydride **5** gave (*R*)-(–)-1,2-diphenylpropan-1-one **10** in yields and enantiomeric excesses dependent on the radical initiator and the experimental conditions (Scheme 3 and Table 1).

9 **10**

Scheme 3

entry	conditions	yield (%)	ee (%)[a]
1	AIBN, 80 °C	70	11
2	AIBN, –78 °C	54	20
3	Et_3B, –78 °C, air[b]	12	30
4	Et_3B, –78 °C, air[c]	13	32
5	Et_3B, –78 °C, N_2[d]	45	25
6	Et_3B, –78 °C, air[e]	35	11
7	Et_3B, –78 °C, air[f]	30	41

Table 1. Yields and enantiomeric excesses of **10** obtained in the reduction of **9** with **5**.

a) Determined by HPLC (see Experimental Section). b) Addition of 30% Et_3B every 2 h for 16 h. c) Addition of 30% Et_3B every 30 min for 4 h. d) Addition of 30% Et_3B every 10 min for 90 min. e) Addition of Et_3B (10 equiv) together with the other reagents. f) Addition of 30% Et_3B every 10 min for 30 min, then 1 h at -78 °C; this result was reproduced 2 times.

When the reaction was carried out at 80 °C with AIBN as a radical initiator, **10** was obtained in good yield but low ee; changing the temperature from 80 °C to –78 °C did not have a dramatic effect on the ee, which raised from 11% to just 20% (Table 1, entries 1 and 2). Better ees were obtained by using triethylborane as a radical initiator.[14] More than a catalytic amount of borane was needed to obtain complete conversion of the starting material, and prolonging the addition of the initiator simply resulted in longer reaction times, a symptom that the chain length is very short (Table 1, entries 3 and 4). Under these conditions, the yield is very low,[15] but the ee is higher. To improve the yields, the same reaction was carried out under a nitrogen atmosphere, since it is known that even trace amounts of oxygen in the solvent can allow triethylborane to start the chain.[14] This reaction did afford **10** in better yield (45%) but, surprisingly, in lower ee (25%, Table 1, entry 5). Other experiments performed under nitrogen or air atmosphere confirmed that a better ee was obtained when the reaction was carried out under air. Although not confirmed, it is possible that the formation of the boron enolate of **10** is responsible for some of the differences in ee.[16] The result in entry 6 is consistent with this postulate: the addition of a large excess of triethylborane at the beginning of the reaction, conditions that should favor the formation of a boron enolate, caused the ee to drop to 11%. Finally, by addition under air of 4 equivalents of triethylborane over 5 h, the reduced product **10** was obtained in better yield and a 41% ee (Table 1, entry 7). Though far from satisfactory, this is the highest selectivity ever obtained in this kind of transformation. The borane plays an undefined but crucial role in the reaction: a similar effect has been observed in the asymmetric radical addition to α-sulfinylcyclopentenones, whose stereochemical course is affected by a change in the size of the borane.[3c]

Whether or not **5** emerges as a useful chiral tin hydride, the synthesis of this parent of the binaphthyl tin hydride class should serve to prepare analogous chiral reagents for use in both radical and ionic chemistry. Studies are underway to investigate the effect of Lewis acids in these reductions and to extend the use of hydrides **4** to other kinds of substrates and reactions.

EXPERIMENTAL SECTION

General procedures. THF, benzene, and toluene were distilled from sodium/benzophenone before use. HPLC analyses were carried out on a Waters 590 instrument equipped with a Regis (*S,S*) Whelk-0 1 chiral column (25 cm x 4.6 mm I.D.) and a Waters R401 differential refractometer using hexane/2-propanol mixtures as eluant and a flow rate of 1 ml/min. AIBN was purified by dissolving in chloroform and reprecipitating with methanol. (*S*)-2,2'-Bis(bromomethyl)-1,1'-binaphthyl **6**,[10] and 2-bromo-1,2-diphenyl-propan-1-one[13] were prepared according to the literature.

(S)-4,4-Dibromo-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]stannepin **7**. [11c] A mixture of **6** (2.20 g, 5 mmol) and tin powder (100 mesh, 1.19 g, 10 mmol) in toluene (60 ml) containing 27 µl of water was refluxed under a nitrogen atmosphere for 5 h. After cooling, the tin powder was filtered and washed with toluene; the organic solutions were combined and the solvent evaporated. The solid residue was suspended in ether (10 ml), it was stirred for a few minutes and filtered to give 2.30 g (82%) of **7**, mp = 260-270 °C (dec.), lit.[11c] mp = 240 °C (dec.); $[\alpha]_D^{25}$ = –163.1° (c 0.58, $CHCl_3$), lit.[11c] $[\alpha]_D^{25}$ = –153.46° (c 0.58, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 2.98 [2H, d, *J* = 11.3 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 76.5 Hz], 3.29 [2H, d, *J* = 11.3 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 76.5 Hz], 7.02 (2H, d, *J* = 8.4 Hz), 7.25 (2H, m), 7.45 (2H, m), 7.55 (2H, d, *J* = 8.5 Hz), 7.94 (4H, m); MS *m/e* (rel. inten.) 564 (M^+ + 6, 0.5), 562 (M^+ + 4, 2), 560 (M^+ + 2, 3), 558 (M^+, 3), 556 (2), 554 (0.5), 280 (100), 279 (81), 278 (29), 277 (33), 276 (35). HRMS calcd for $C_{22}H_{16}{}^{79}Br_2{}^{120}Sn$ 557.8461, found 557.8625; HRMS calcd for $C_{22}H_{16}{}^{79}Br^{81}Br^{120}Sn$ 559.8620, found 559.8633.

(S)-4-Bromo-4,5-dihydro-4-methyl-3H-dinaphtho[2,1-c:1',2'-e]stannepin **8**. Trimethylaluminum (2.0 M solution in toluene, 0.89 ml, 1.79 mmol) was added dropwise at 25 °C under a nitrogen atmosphere to a stirred solution of **7** (1.0 g, 1.79 mmol) in dry THF (25 ml). The resulting solution was stirred for additional 30 min and then it was poured into 4% aqueous hydrobromic acid and extracted with ether and methylene chloride. The combined organic phases were dried over magnesium sulfate and the solvent was evaporated. The solid residue was suspended in ether (3-4 ml) and stirred for a few minutes; after filtration, the title compound was obtained in 86% yield, mp = 208-218 °C; $[\alpha]_D^{25}$ = –150.8 (c 0.5, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 0.82 [3H, s, ^2J ($^{117/119}$Sn, ^{1}H) = 52.1 Hz], 2.45 [1H, d, *J* = 11.6 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 42.6 Hz], 2.51 [1H, d, *J* = 11.2 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 103.7 Hz], 2.76 [1H, d, *J* = 11.6 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 54.4 Hz], 2.84 [1H, d, *J* = 11.2 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 40.0 Hz], 7.00 (1H, d, *J* = 8.4 Hz), 7.08 (1H, d, *J* = 8.4 Hz), 7.15-7.28 (2H, m), 7.35-7.50 (3H, m), 7.53 (1H, d, *J* = 8.5 Hz), 7.85-7.98 (4H, m); ^{13}C-NMR ($CDCl_3$) δ -1.02 [^1J (^{117}Sn, ^{13}C) = 249.0 Hz, ^1J (^{119}Sn, ^{13}C) = 259.0 Hz], 23.50 [^1J (^{117}Sn, ^{13}C) = 302.7 Hz, ^1J (^{119}Sn, ^{13}C) = 317.3 Hz], 24.56 [^1J (^{117}Sn, ^{13}C) = 303.1 Hz, ^1J (^{119}Sn, ^{13}C) = 317.3 Hz], 124.88, 125.20, 125.98, 126.23, 126.34, 126.42, 126.73, 127.73, 128.18, 128.28, 128.51, 128.99, 131.90, 132.00, 132.39, 132.91, 133.39, 134.88, 135.65; MS *m/e* (rel. inten.) 498 (M^+ + 4, 1), 496 (M^+ + 2, 7), 495 (M^+ + 1, 3), 494 (M^+, 11), 493 (3), 492 (4), 490 (2), 280 (62), 279 (100), 278 (40), 277 (45), 276 (54), 265 (20), 263 (21), 252 (16). HRMS calcd for $C_{23}H_{19}{}^{79}Br^{120}Sn$ 493.9692, found 493.9686.

(S)-4,5-Dihydro-4-methyl-3H-dinaphtho[2,1-c:1',2'-e]stannepin **5**. The alane solution was prepared according to the literature[17] from $LiAlH_4$ (1.0 M solution in THF, 5 ml, 5 mmol) and conc. sulfuric acid (d = 1.84 g/ml, 0.14 ml, 2.5 mmol) in THF (25 ml). This solution (1.2 ml, 0.2 mmol) was added dropwise at 0 °C under a nitrogen atmosphere to a stirred solution of **8** (99 mg, 0.2 mmol) in THF (10 ml). The resulting mixture was stirred at 25 °C for 1 h, then poured into a saturated aqueous potassium sodium tartrate

solution (30 ml) and extracted with ether. The organic phase was dried over magnesium sulfate and the solvent evaporated to give 95% of the title compound, mp ≅ 220 °C;[18] $[\alpha]_D^{25}$ = +100.1 (c 0.76, benzene); ^{1}H-NMR (benzene-d_6) δ -0.06 [3H, d, J = 2.1 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 36.2 Hz], 1.83 [1H, dd, J_1 = 11.1 Hz, J_2 = 1.9 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 76.4 Hz], 1.84 [1H, dd, J_1 = 11.1 Hz, J_2 = 2.5 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 76.4 Hz], 2.06 [1H, d, J = 11.1 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 75.8 Hz], 2.08 [1H, d, J = 11.1 Hz, ^2J ($^{117/119}$Sn, ^{1}H) = 34.9 Hz], 5.78 (1H, bm, Sn-H), 6.97 (2H, ddd, J_1 = J_2 = 6.9 Hz, J_3 = 1.7 Hz), 7.10-7.20 (3H, m), 7.22-7.35 (3H, m), 7.68-7.80 (4H, m); ^{119}Sn-NMR (benzene-d_6) δ 119.76 (doublet of multiplets, J = 1778.7 Hz); IR (film, NaCl plates) 3044, 3004, 2982, 2967, 2927, 1825 (vs, Sn-H stretch), 1614, 1591, 1505, 1353. 1330, 1236, 1079, 820, and 747 cm^{-1}; MS *m/e* (rel. inten.) 416 (M^+, 25), 415 (18), 414 (21), 413 (14), 412 (12), 401 (100), 400 (59), 399 (82), 398 (51), 397 (58), 279 (48), 278 (32), 277 (44), 276 (54), 266 (46), 265 (62), 264 (26), 263 (38), 252 (17), 239 (8). HRMS calcd for $C_{23}H_{20}{}^{120}Sn$ 416.0587, found 416.0569.

General Procedure for the Reduction of **9** *with* **5**. The reactions were carried out with **9** (0.08 mmol) and **5** (0.18 mmol) in 0.8 ml of benzene (reaction at 80 °C) or toluene (reactions at -78 °C). In the reaction with AIBN at -78 °C (Table 1, entry 2), the solution was irradiated with a 450-W high-pressure mercury lamp for 6 h, and additional AIBN (3 mg) was added every 2 h. In the reactions at -78 °C under air (Table 1, entries 3, 4, 6, and 7), the toluene solution of the reactants was cooled to -78 °C under a nitrogen atmosphere. Then the nitrogen flow was stopped and a very slow dry-air flow was bubbled into the reaction mixture for 5 min; Et_3B (0.3 equiv) was added and the resulting mixture stirred at -78 °C under an air atmosphere. The reaction times and the ways of addition of the borane are described for each reaction in Table 1. After workup and chromatography (silica gel, hexanes/diethyl ether 98:2 v/v), the fraction containing **10** was analyzed by HPLC to obtain the enantiomeric excess (2-propanol/hexane 1:99 v/v as eluant, t_R of (*S*)-(+)-**10** = 8.3 min, t_R of (*R*)-(–)-**10** = 11.8 min). Pure (*R*)-(–)-**10**[19] was proved to be optically stable under all of the reaction conditions.

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12) Alkylation of **7** was surprisingly difficult to achieve. The reaction with a Grignard reagent afforded a very complicated mixture of unidentified products. A redistribution reaction with tetramethyltin gave mixtures of **7** and **8**; attempts to drive the reaction to completion led to decomposition of both compounds. Likewise, among the reducing agents surveyed, only alane provided a clean product.
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