atom[1, 4] is in good agreement with the radical abstraction and recombination process outlined in Scheme 2.[20] In the course of the disproportionation of the benzylic radical (β-cleavage) into the olefin, the ensuing alkyloxy or acyloxy radical will immediately recombine with the neighboring porphyryl-Fe^{IV}-OH center to avoid formation and escape of free radicals.

The oxidative bond cleavage reaction described here may also be representative for ring-cleavage reactions in the biosynthesis of seco compounds that are, as yet, not systematically addressed on mechanistic grounds. For example, the transformation of loganin into secologanin, a central step in the biosynthesis of indole and chinchona alkaloids, apparently proceeds without intermediates and is catalyzed by a cytochrome P450.[22] Comparable reactions take place in the oxidative cleavage of ring A of the triterpenoid β-amyrin to provide nyctanthic acid[23] or the oxidative degradation of acyclic geranylacetone to 4,8-dimethyl-1,3,7-nonatriene. The latter transformation is exceptionally widespread in higher plants in response to herbivory.[24] The recent finding that the acyclic geranylacetone is degraded by *syn* elimination[24, 25] strongly supports the significance of this unique stereochemical feature of cytochrome P450 catalyzed oxidative bond cleavage reactions.

Experimental Section

Enzymatic conversions were performed with microsomes from elicited cell cultures of *Ammi majus*.[14] The labeled marmesin derivatives[13] (40.0 nmol) were dissolved in Tris/HCl buffer (25.0 μL, 50.0 mM, pH 7.5) containing EDTA (1.0 mM) and NADPH (10.0 μL of a 10.0 mM solution in the same buffer), and a suspension of the microsomes (20.0 μL) was added. After 30 min at 20 °C the reaction products were isolated by solid-phase microextraction (SPME, fiber coated with polymethyldisiloxane).[26] Equilibrium was reached after 30 min of extraction, and the products were then evaporated (250 °C) from the fiber in the injection port of the GC-MS instrument (GC-MS: Fisons MD 800, column: SE 30, 10 m × 0.31 mm, carrier gas: He, temperature program: 50 °C (2 min) to 280 °C at 20 °C min^{-1}, interface: 270 °C, mass range: 35–350 Da sec^{-1}). In each experiment about 5% of the substrates **3a**, **3b**, **4**, or **7** were transformed. To facilitate the analysis of acetone and [$^2H_6$]acetone, the reaction mixture was treated prior to extraction with 5.0 μL of a 0.1 mM solution of pentafluorobenzylhydroxylamine in Tris/HCl buffer.[15] Formation of the amine was complete after 30 min. Following derivatization, acetone and psoralen could be quantified by GC-MS. Calibration was achieved with authentic references prepared from acetone and [$^2H_6$]acetone.

In the model reactions solutions of the metalloporphyrinato complex (Fe^{3+} or Mn^{3+}, 1.4 mmol) and the deuterated (±)-marmesins **3a**, **3b, 4**, and **7** (8.1 mmol) in dichloromethane (3.0 mL) were stirred with iodosylbenzene (22.0 mmol) at 4 °C for 8 h. The products were analyzed by GC-MS without further workup. About 10% of the substrate was transformed. The carbonyl fragment was detected as described above as the pentafluorobenzylhydroxylamine.[15]

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Transmetalation of Tetraalkynyltin Compounds with Grignard Reagents: Access to Mono- and Dialkyltin Products

Pascale Jaumier, Bernard Jousseaume,* and Mohammed Lahcini

The transmetalation of organotin compounds with lithium reagents[1] provides access to allyl-[1], vinyl-,[2] and α-heteroalkyllithium reagents,[3] especially for applications in organic synthesis.[4] Recent examples of other such transmetalation reactions involved palladium,[5] copper,[6] and boron compounds.[7] In these reactions [Eq. (1)], the organic group that

$$R^1_3SnR^2 + R^3M \longrightarrow R^2M + R^1_3SnR^3 \quad (1)$$

[*] Dr. B. Jousseaume, Dr. P. Jaumier, Dr. M. Lahcini
Laboratoire de Chimie Organique et Organométallique
UMR 5802, Université Bordeaux I
351 Cours de la Libération, F-33405 Talence Cedex (France)
Fax: (+33) 5-56-84-6994
E-mail: b.jousseaume@lcoo.u-bordeaux.fr

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is transferred from tin to the other metal is the important part of the molecule, whereas the tetraorganotin compound (or the triorganotin halide in the case of the Stille reaction[5]) is a secondary product.

On the other hand, there is no general route to monoorganotin compounds from an organometallic derivative and an inorganic tin compound such as tin tetrachloride. Alkylation or arylation leads to mixtures of mono-, di-, tri-, and tetraorganotin compounds, even when only one equivalent of alkylating (or arylating) agent is used.[8] This is in contrast to silicon,[9] for which monoalkylation (or arylation) is easy. Monoorganotin compounds are usually prepared from unsymmetrical or symmetrical tetraorganotin compounds by electrophilic cleavage of three reactive organic groups with halogens, protic acids, or tin tetrahalides. Some other methods are limited to specific substrates, mainly those with a β- or γ-carbonyl substituent.[10] In our studies on trichloroorganotin compounds in which the organic moiety bears a polymerizable group,[11] a direct route to monoorganotin compounds that avoids the use of hydrochloric acid or tin tetrachloride, which can react with the polymerizable group, was essential.

Monotransmetalation of tetraaryl-, tetraallyl-, or tetraalkynyltin with one equivalent of butyllithium in diethyl ether or THF at different temperatures did not give any selective reactions. Mixtures of mono-, di-, tri-, and tetrabutyltin were invariably obtained. The use of Grignard reagents was more successful. When tetrapropyn-1-yltin was treated with one equivalent of *n*-butylmagnesium bromide in diethyl ether, *n*-butyltripropyn-1-yltin was obtained [Eq. (2)] in 68% yield with a purity of 95% (Table 1). It was purified by chromatography on dry Florisil or by recrystallization.[12, 13]

$$(MeC{\equiv}C)_4Sn + n\text{BuMgBr} \longrightarrow (MeC{\equiv}C)_3Sn n\text{Bu} + MeC{\equiv}CMgBr \qquad (2)$$

The reaction was extended to methyl-, isopropyl-, and *tert*-butylmagnesium halides with equal success (Table 1). Iodides reacted more slowly than the corresponding chlorides and bromides, and the highest selectivities and yields were obtained with tetrakis(phenylethynyl)tin. Selectivity was equally good in diethyl ether and THF, but THF induced slightly higher reaction rates, as is observed for lithium reagents.[14] In THF, higher reaction temperatures allowed some more reluctant transmetalations, especially with secondary or tertiary organomagnesium compounds, to be performed.

Moreover, the reaction was successfully extended to two successive transmetalations to give dialkyltin dialkynides when two equivalents of Grignard reagent were used [Eq. (3), Table 1]. Thus, Grignard reagents are able to

$$(MeC{\equiv}C)_4Sn + 2\,n\text{BuMgBr} \longrightarrow (MeC{\equiv}C)_2Sn n\text{Bu}_2 + 2\,MeC{\equiv}CMgBr \qquad (3)$$

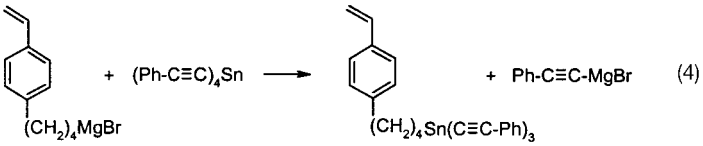
discriminate between tetraalkynyltin, alkyltrialkynyltin, and dialkyldialkynyltin compounds; the electronic effects of the alkyl groups probably induce a sharp difference in the electrophilic properties of the tin atom with respect to the nucleophilic organomagnesium compounds. In contrast, phenyl and allyl groups, which have acceptor properties, do not lead to any selectivity: phenylmagnesium bromide and tetrakis(phenylethynyl)tin gave mono- and diarylation products in equal amounts, and allylmagnesium bromide and tetrakis(phenylethynyl)tin furnished a mixture of mono-, di-, and triallyl derivatives.

Table 1. Alkyltrialkynyl- and dialkyldialkynyltin compounds obtained from tetraalkynyltin starting materials.

Starting material[a]	Product	Solvent	Purity [%][b]	Yield [%]
$(MeC{\equiv}C)_4Sn$	$(MeC{\equiv}C)_3SnMe$[21]	Et_2O	85	41
$(MeC{\equiv}C)_4Sn$	$(MeC{\equiv}C)_3Sn n\text{Bu}$[21]	Et_2O	95	68
$(MeC{\equiv}C)_4Sn$	$(MeC{\equiv}C)_3Sn i\text{Pr}$	Et_2O	88	70
$(BuC{\equiv}C)_4Sn$	$(BuC{\equiv}C)_3Sn n\text{Bu}$[22]	Et_2O	92	43
$(PhC{\equiv}C)_4Sn$	$(PhC{\equiv}C)_3SnMe$[23]	Et_2O	100	87
$(PhC{\equiv}C)_4Sn$	$(PhC{\equiv}C)_3Sn n\text{Bu}$[24]	Et_2O	100	75
$(PhC{\equiv}C)_4Sn$	$(PhC{\equiv}C)_3Sn i\text{Pr}$	THF	95	89
$(PhC{\equiv}C)_4Sn$	$(PhC{\equiv}C)_3Sn t\text{Bu}$	THF	100	82
$(MeC{\equiv}C)_4Sn$	$(MeC{\equiv}C)_2Sn n\text{Bu}_2$[25]	Et_2O	93	70
$(BuC{\equiv}C)_4Sn$	$(BuC{\equiv}C)_2Sn n\text{Bu}_2$[22]	Et_2O	85	38
$(PhC{\equiv}C)_4Sn$	$(PhC{\equiv}C)_2Sn i\text{Pr}_2$	THF	86	75

[a] Consumption of the starting material was in the range of 95–100%. [b] Percentage monoalkylation or dialkylation. By-products were dialkylation compounds in monoalkylation reactions and monoalkylation compounds in dialkylation reactions.

From a practical point of view, this method is particularly interesting for the preparation of monoorganotin compounds when the corresponding trichlorides are unstable, as in the case, for instance, of *tert*-butyltrichlorotin,[15] which decomposes to tin dichloride and *tert*-butyl chloride at room temperature, and (ω-styrylalkyl)trichlorotin compounds, which spontaneously oligomerize as soon as they are formed.[16] Labile tin–alkynyl bonds allow the transformation of tetraorganotin compounds into stable but reactive monoorganotin compounds that can undergo further reactions (alkylation, reduction, halogenation, etc.) as trialkoxides or oxides after reaction with alcohols or water.[17] Among these compounds, (ω-styrylalkyl)trialkynyltin compounds [Eq. (4)],



(4)

which are easily transformed into the corresponding oxides, are good candidates for the preparation of new tin-based[18] organic–inorganic hybrid materials.

The secondary and tertiary alkyltrialkynyltin compounds are as reactive as the primary compounds. Isopropyltriphenylethynyltin gave the corresponding trichloride[19] on treatment with HCl/MeOH, and hydrolysis of *tert*-butyltriphenylethynyltin led to the corresponding oxide.[20]

Aryl groups are also displaced from tin by Grignard reagents. When one equivalent of tetraphenyltin was treated with four equivalents of methylmagnesium chloride in THF at reflux for 16 h, methyltriphenyltin (54%) was formed together with dimethydiphenyltin (6%); 40% of the tetraphenyltin remained unchanged. Transmetalation can thus occur with groups that are more strongly bonded to tin than alkynyl

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moities. However the reaction is more difficult and less selective.

We have demonstrated that transmetalation of tetraorganotin compounds is not limited to organolithium, -boron, -copper, and palladium compounds, but that it is also possible with Grignard reagents and tetraalkynyltin compounds. In contrast to organolithium reagents, this transmetalation is highly selective and allows the preparation of alkyltrialkynyl and dialkyldialkynyltin compounds and hence provides a new route to monoalkyltin alkoxides, oxides, and halides which avoids strong electrophilic reagents such as halogens, protic acids, or tin tetrahalides.

Experimental Section

The preparation of 4-(4-styryl)butyltris(phenylethynyl)tin is representative: A solution of tetrakis(phenylethynyl)tin (10 mmol, 5.23 g) in dry diethyl ether (20 mL) and toluene (40 mL) was treated with a ca. 1N solution of bromo(4-(4-styryl)butyl)magnesium in diethyl ether (10 mmol) at $-20\,^{\circ}C$. After warming to room temperature, the solution was heated to reflux for 18 h. Then, water (0.5 mL) was added at $-30\,^{\circ}C$, and the mixture treated with dry magnesium sulfate (5 g). After filtration and evaporation of the solvents under vacuum, rapid chromatography on dry Florisil gave 4-(4-styryl)butyltris(phenylethynyl)tin in 60% yield. M.p. 72 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.42$ (t, 2H, ^3J(H,H) = 7.2, ^2J(Sn,H) = 61 Hz), 1.62–1.80 (m, 4H), 2.54 (t, 2H, ^3J(H,H) = 7.2 Hz), 5.06 (d, 1H, ^3J(H,H) = 10.9 Hz), 5.54 (dd, 1H, ^3J(H,H) = 17.5), 6.54 (dd, 1H, ^3J(H,H) = 17.5, 10.9 Hz), 6.92–7.48 (m, 19H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.9$ (^1J(Sn,C) = 640 Hz), 24.5 (^2J(Sn,C) = 35 Hz), 33.9 (^3J(Sn,C) = 81 Hz), 34.7, 84.7 (^1J(Sn,C) = 798 Hz), 110.5 (^2J(Sn,C) = 165 Hz), 113.2, 123.1, 126.7, 129.1, 129.3, 129.4, 132.9, 135.8, 137.4, 142.7; ^{119}Sn NMR (74.6 MHz, $CDCl_3$): $\delta = -242$; elemental analysis calcd for $C_{36}H_{30}Sn$: C 74.38, H 5.20; found: C 73.6, H 5.1.

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[20] ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.33$ (s, 4.5H, ^3J(Sn,H) = 137 Hz), 1.52 (s, 4.5H, ^3J(Sn,H) = 151 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta =$ 30.3 (1.5C, ^2J(Sn,C) = 20 Hz), 31.3 (1.5C, ^2J(Sn,C) = 21 Hz), 41.8 (0.5C, ^1J(Sn,C) = 900 Hz), 42.7 (0.5C, ^1J(Sn,C) = 1250 Hz); ^{119}Sn NMR (74.6 MHz, $CDCl_3$): $\delta = -336.7$ (0.5Sn), -495.2 (0.5Sn).
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