

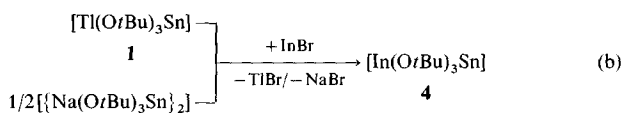


Table 1. Results of the X-ray structure analyses of 3, 4, 8, and 10 [2].

	4	3	8	10
Crystal system	hexagonal	monoclinic	orthorhombic	monoclinic
Space group	$P6_3/m$	$P2_1/n$	$Pnma$	$P2_1/n$
Z	2	4	4	4
a [Å]	9.867(9)	9.952(8)	15.11(1)	10.51(1)
b [Å]	9.867(9)	17.59(1)	14.17(1)	30.30(2)
c [Å]	11.21(1)	15.11(1)	15.76(1)	10.748(7)
Angle [°]	$\gamma = 120$	$\beta = 100.20(7)$	–	$\beta = 107.36(7)$
In–O [Å] (TI–O)	2.413(4)	2.557(15)	2.141(6)	2.21(1)
Sn–O [Å]	2.032(4)	2.017(9)	2.122(9)	2.07(1)
Sn–Mo [Å]	–	2.770(2)	2.761(1)	–
Sn–Cr [Å]	–	–	–	2.636(3)
In–Mo [Å]	–	–	2.742(1)	2.734(2)
O–In–O [°] (O–TI–O)	66.7(1)	63.9(8)	73.2(3)	70.6(5)
O–Sn–O [°]	81.5(1)	84.2(9)	74.0(3)	76.6(5)
In...Sn [Å] (TI)	3.200(3)	3.298(1)	3.078(1)	3.087(2)
R value	0.037	0.062	0.058	0.068

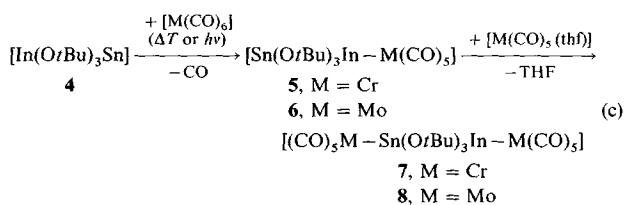
Compared with the starting compound **1** (Sn–O = 2.023(9), TI–O = 2.595(7), and TI...Sn = 3.306(2) Å<sup>[11]</sup>), all metal–oxygen distances are slightly shortened; the distance between thallium and tin is decreased. Characteristic of the monoadducts **2** and **3** are the high CO wave numbers ( $\nu(A_1^{1b})$  bands) and a strong downfield shift of the <sup>119</sup>Sn NMR signals relative to those of compound **1** ( $\Delta\delta = 97.04$ ; Table 2). Even under drastic conditions (large excess of metal carbonyl, higher temperature, longer reaction time), no complex fragment becomes bonded to the thallium atom of **2** or **3**.

We therefore attempted to replace thallium by its homologue indium. The desired compound **4** may be obtained starting either from **1** or from the sodium salt [ $\{Na(OrBu)_3Sn\}_2$ ]<sup>[3]</sup> in a heterogeneous reaction with InBr [Eq. (b)].



Toluene, used as solvent, apparently causes partial dissolution of InBr via formation of an arene complex.<sup>[4]</sup> The monomeric product **4**, like **1**, is soluble in nonpolar solvents, exhibits a similar <sup>119</sup>Sn absorption (Table 2), and forms isotopic crystals (Table 1). According to an X-ray structure analysis, **4** has a distorted bipyramidal InO<sub>3</sub>Sn structure with In and Sn in apical positions and the three oxygens in equatorial positions. Compared with **1**, the indium atom is closer to the O<sub>3</sub> plane than the thallium atom, as expected; the distances to the oxygen atoms lie in the normal range (see also indium 2,4,6-tris(trifluoromethyl)phenoxide<sup>[5]</sup>).

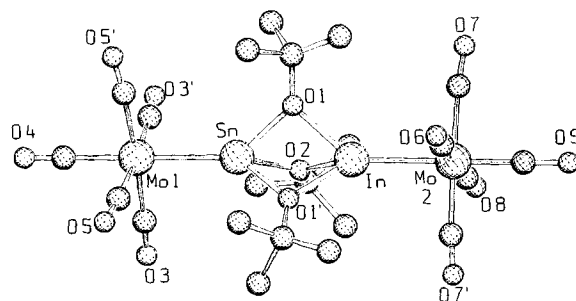
Reaction of **4** with [Cr(CO)<sub>6</sub>] or [Mo(CO)<sub>6</sub>] in THF either thermally or photochemically in analogy to Equation (a) likewise results in formation of monoadducts **5** and **6**, respectively. Use of an excess of the metal carbonyl or longer reaction times results in further reaction to give the diadducts **7** and **8**, respectively [Eq. (c)].



In contrast to **2** and **3**, the transition-metal atoms in **5** and **6** are not coordinated to the tin atom but rather to the indium atom. This is revealed by the upfield shift of the <sup>119</sup>Sn NMR signal (**6**:  $\Delta\delta = -95.96$ ) compared with that of **4** and by the wave numbers of the  $\nu(A_1^{1b})$  stretching band, which indicate a different electron density *trans* to the CO group (see Table 2).

This is shown especially clearly on going from the monoadducts **5** and **6** to the diadducts **7** and **8**. The second  $\nu(A_1^{1b})$  bands due to the M(CO)<sub>5</sub> units on tin lie in the absorption region observed for compounds **2** and **3** (Table 2).

The result of an X-ray structure analysis of **8** is shown in Figure 2. The four metal atoms Mo, Sn, In, and Mo are

Fig. 2. Molecular structure of **8** [2] (atoms labeled as in Fig. 1). The stacked arrangement of the Mo(CO)<sub>5</sub> groups is clearly shown.

arranged nearly linearly (Mo–Sn–In = 174.2°, Mo–In–Sn = 178.8°), with metal single bonds between Mo and In and between Mo and Sn (distances in Table 1); as found in the starting compound **4**, In and Sn are bridged by three *tert*-butoxy groups. The coordination of Mo(CO)<sub>5</sub> units on indium and tin results in withdrawal of electron density from indium, so that the In–O distance is significantly less than that in **4**. The electron density on Sn is increased to a comparable extent; that is, the Sn–O distances are longer than those in free **4**. If the whole molecule is considered, however, **4** acts as an electron donor toward the Mo(CO)<sub>5</sub> units, since the In...Sn distance in **8** is less than that in **4** by 0.122 Å (Table 1).

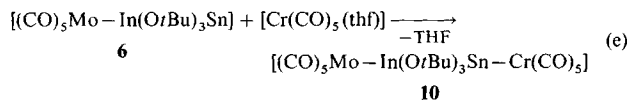
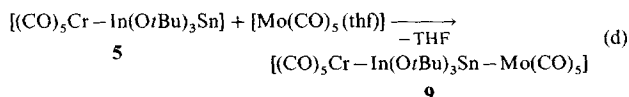
The preferential coordination of the fragments [Cr(CO)<sub>5</sub>] and [Mo(CO)<sub>5</sub>] to indium in the monoadducts can be ex-

Table 2. <sup>1</sup>H and <sup>119</sup>Sn NMR data ( $\delta$  values in benzene) and CO wave numbers [cm<sup>-1</sup>] for compounds 1–10.

	$\delta(^1H)$	$\delta(^{119}Sn)$	$\nu(A_1^{1b})$	$\nu$ (other CO)
[TI(OrBu) <sub>3</sub> Sn] <b>1</b>	1.32	-78.72[a]	–	–
[In(OrBu) <sub>3</sub> Sn] <b>4</b>	1.37	-77.27	–	–
[TI(OrBu) <sub>3</sub> Sn–Cr(CO) <sub>5</sub> ] <b>2</b>	1.31	–	2060 (m)	1970 (sh) 1920 (vs)
[TI(OrBu) <sub>3</sub> Sn–Mo(CO) <sub>5</sub> ] <b>3</b>	1.31	+18.32	2070 (m)	1980 (sh) 1930 (vs)
[Sn(OrBu) <sub>3</sub> In–Cr(CO) <sub>5</sub> ] <b>5</b>	1.23	–	2033 (m)	1968 (w) 1913 (vs)
[Sn(OrBu) <sub>3</sub> In–Mo(CO) <sub>5</sub> ] <b>6</b>	1.23	-173.23	2051 (m)	1925 (vs)
[(CO) <sub>5</sub> Cr–Sn(OrBu) <sub>3</sub> In–Cr(CO) <sub>5</sub> ] <b>7</b>	1.27	–	2058 (m)	1975 (sh) 2041 (m) 1925 (vs, br)
[(CO) <sub>5</sub> Mo–Sn(OrBu) <sub>3</sub> In–Mo(CO) <sub>5</sub> ] <b>8</b>	1.28	–	2069 (m)	1965 (s) 2050 (m) 1915 (vs, br)
[(CO) <sub>5</sub> Cr–In(OrBu) <sub>3</sub> Sn–Mo(CO) <sub>5</sub> ] <b>9</b>	1.28	–	2069 (m)	1978 (sh) 2033 (m) 1950 (vs) 1930 (vs) 1912 (vs)
[(CO) <sub>5</sub> Mo–In(OrBu) <sub>3</sub> Sn–Cr(CO) <sub>5</sub> ] <b>10</b>	1.28	–	2059 (m)	1975 (sh) 1930 (vs) 1912 (vs)

[a]  $J(^{205}, ^{203}TI-Sn) = 1293$  Hz.

plotted chemically. As shown in Equations (d) and (e) reaction of **5** and **6** with the THF adduct of the corresponding metal pentacarbonyl affords the positional isomers **9** and **10**, respectively, which contain four different metal atoms.



Compounds **9** and **10** are clearly distinguished by their CO wave numbers (Table 2) and crystal data (Table 1).<sup>[6]</sup> The X-ray structure analysis of **10** (Fig. 3, Table 1) again reveals

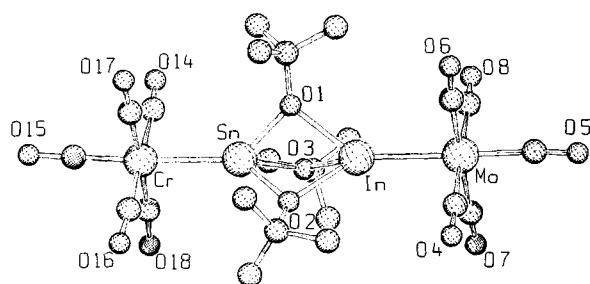


Fig. 3. Molecular structure of **10** [2]. In contrast to **8**, the  $\text{M}(\text{CO})_5$  groups are arranged in an eclipsed fashion.

an almost linear arrangement of the metal atoms ( $\text{Mo}-\text{In}\cdots\text{Sn} = 178.1(1)^\circ$ ,  $\text{Cr}-\text{Sn}\cdots\text{In} = 179.7(1)^\circ$ ). Interchange of the Sn and In positions in the structure analysis leads here and for **8** to poorer  $U$  values. As found for **8**, addition of  $[\text{M}(\text{CO})_5]$  fragments to **4** results in a decrease in the separation of the main-group metals ( $\Delta d = 0.113 \text{ \AA}$ ) and a charge shift from indium to tin. However, owing to the shorter Cr–Sn bond compared with the Mo–Sn bond in **8**, the charge shift is less pronounced.

#### Experimental Procedure

**4**:  $[\text{Ti}(\text{OrBu})_3\text{Sn}]$  (1.0 mmol) [**1**] or  $[\{\text{Na}(\text{OrBu})_3\text{Sn}\}_2]$  (0.5 mmol) [**3**] was stirred with indium(I) bromide (1.4 mmol) in 15 mL of toluene at  $110^\circ\text{C}$  for 5 or 40 h, respectively. The insoluble material, which may contain some indium, was removed by filtration and the filtrate was concentrated. Sublimation of the residue at  $30^\circ\text{C}/10^{-2}$  Torr afforded 0.42 g (92%) or 0.41 g (90%), respectively, of **4**; m.p.  $41^\circ\text{C}$ .

**2**, **3**, and **5**–**10**: A stirred solution of **1** or **4** and  $[\text{Cr}(\text{CO})_6]$  or  $[\text{Mo}(\text{CO})_6]$  in toluene was heated to reflux. Alternatively, the metal carbonyl was first photolyzed in THF and then allowed to react with **1** or **4** in toluene. Preparation of **9** and **10** starts with **5** and **6**, respectively, whose synthesis must be carried out with exact molar ratios of starting materials. All of the compounds were purified by sublimation or recrystallization and gave correct elemental analyses (C, H, metal).

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**1**, 83437-08-5; **2**, 131010-15-6; **3**, 131010-16-7; **4**, 131010-17-8; **5**, 131010-18-9; **6**, 131010-19-0; **7**, 131010-20-3; **8**, 131010-21-4; **9**, 131010-22-5; **10**, 131010-23-6;  $[\text{Cr}(\text{CO})_6]$ , 13007-92-6;  $[\text{Mo}(\text{CO})_6]$ , 13939-06-5;  $[\text{Na}(\text{OrBu})_3\text{Sn}]$ , 105803-03-0;  $[\text{Cr}(\text{CO})_5(\text{thf})]$ , 15038-41-2;  $[\text{Mo}(\text{CO})_5(\text{thf})]$ , 53248-43-4; In, 7440-74-6; Mo, 7439-98-7; Cr, 7440-47-3; Sn, 7440-31-5.

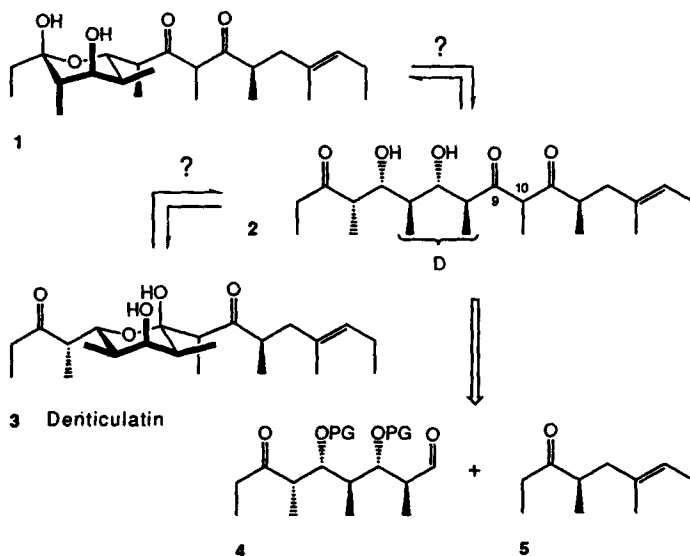
[1] M. Veith, R. Rösler, *Angew. Chem.* 94 (1982) 867; *Angew. Chem. Int. Ed. Engl.* 21 (1982) 858.

- [2] Further details of the crystal structure investigations of **3**, **4**, **8**, and **10** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-54897, the names of the authors, and the journal citation.
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- [5] M. Scholz, M. Noltemeyer, H. W. Roesky, *Angew. Chem.* 101 (1989) 1419; *Angew. Chem. Int. Ed. Engl.* 28 (1989) 1383.
- [6] Compound **9** forms orthorhombic crystals, space group  $Pnma$ ,  $a = 14.93(2)$ ,  $b = 14.33(2)$ ,  $c = 15.46(2) \text{ \AA}$ .
- [7] M.p., b.p., yield: **2**,  $104^\circ\text{C}$ ,  $40^\circ\text{C}/10^{-3}$  Torr, 50%; **3**,  $107^\circ\text{C}$ ,  $45^\circ\text{C}/10^{-3}$  Torr, 70%; **5**,  $101^\circ\text{C}$ ,  $44^\circ\text{C}/10^{-3}$  Torr, 50%; **6**,  $103^\circ\text{C}$ ,  $50^\circ\text{C}/10^{-3}$  Torr, 25%; **7**,  $148^\circ\text{C}$  (dec.), –, 80%; **8**,  $150^\circ\text{C}$  (dec.), –, 64%; **9**,  $143^\circ\text{C}$  (dec.), –, 58%; **10**,  $145^\circ\text{C}$  (dec.), –, 75%.
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## Efficient Stereoselective Total Synthesis of Denticulatins A and B\*\*

By Marc W. Andersen, Bernhard Hildebrandt, and Reinhard W. Hoffmann\*

The stereoselective synthesis of natural products of polyketide origin, particularly those which contain the stereotriad D, remains a challenge to the preparative chemist.<sup>[1]</sup> Among such substances are the denticulatins **3**,<sup>[2]</sup> two polypropionates isolated from *Siphonaria*, whose biological significance remains unclear. Denticulatin is a polyhydroxy-polyketo compound and exists in the form of a semiacetal. For the synthesis of the denticulatins it is of interest whether open-chain precursors such as **2** cyclize to the correct denticulatin isomer **3**, as well as whether other semiacetals such as **1** isomerize to the desired product (Scheme 1).



Scheme 1. Possible synthetic routes to denticulatin. PG = protecting group.

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