the complete connectivity pattern.[20] This technique of spectral assignment requires no knowledge of the biosynthetic distribution of label since it depends exclusively on increasing the level of ^{13}C in the molecule. However, intact biosynthetic units can still be identified because there is a much higher level of coupled signals between carbons comprising them if multiply ^{13}C-labeled precursors are used.[21] Bacher, Floss, and co-workers recently demonstrated[22] the utility of double-quantum coherence NMR for biosyntheses employing [U-$^{13}C_6$]glucose as a presursor.[23]

Incorporations[18] of sodium [1-^{13}C]acetate, sodium [2-^{13}C]-acetate, and [*methyl*-^{13}C]methionine followed by ^{13}C NMR analysis showed that the main portion of mevinolin (**1**) consists of a polyketide chain of nine intact acetate units with a methionine-derived methyl group at C-6 (Figure 1). Interestingly, the α-methylbutyryl side chain is constructed in an analogous fashion. Recent methods to detect oxygen-18[24] or deuterium[13a,25] by isotope shifts induced in ^{13}C NMR provide mechanistic information by limiting possible intermediate oxidation states and revealing precursor bonds to oxygen or hydrogen that remain intact in the product. Administration[18] of sodium [1-^{13}C,$^{18}O_2$]acetate[24b] to cultures of *A. terreus* followed by both normal and SEFT ^{13}C NMR analysis[24b-e] of the resulting mevinolin (**1**) showed extensive labeling of the doubly bonded oxygen at C-1′ (isotope shift 0.038 ppm). Even though ^{13}C incorporation was high (2-7-fold peak enhancement), the amount of oxygen-18 at other expected sites such as C-11, C-13, and C-15 was less than 5% of the carbon labeling. We are currently investigating the problem of solvent-exchange during biosynthesis. Incorporation of sodium [1-^{13}C,$^{2}H_3$]acetate and ^{13}C NMR examination of the β-isotope shifts[25] in mevinolin (**1**) indicated high ^{2}H retention at all expected sites except C-3 and C-6 (Table I). Since the β-isotope shifts may be upfield, downfield, or possibly zero,[25f] there is a small chance that these carbons bear deuterium, but most probably the biogenesis of **1** results in hydrogen loss at these positions. The presence of species bearing three deuteriums at C-4′ and at the C-2 methyl identifies these carbons as starter units of the polyketide chains. These observations were confirmed by ^{2}H NMR of mevinolin (**1**) derived from sodium [$^{2}H_3$]acetate. Our results support biogenesis of **1** either by intramolecular Diels-Alder cyclization of a C-18 polyunsaturated acid or by the more likely mechanism of intramolecular anionic condensations of a partially reduced C-18 polyketide. Work is in progress to elucidate the biochemical details of the formation of mevinolin (**1**) and compactin (**2**).

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Registry No. 1, 75330-75-5; acetic acid, 64-19-7; L-methionine, 63-68-3.

Supplementary Material Available: Listing of ^{1}H NMR data of **1** and conditions for incorporation experiments (1 page). Ordering information is given on any current masthead page.

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First Synthesis of Stannacyclobutanes

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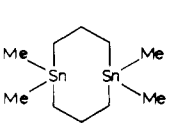
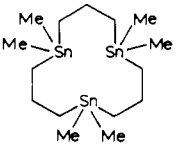
Stannacyclobutanes were hitherto unknown, although their synthesis has been attempted and claimed repeatedly.[1,2] This is all the more remarkable as 1,3-distannacyclobutanes[3] and cyclotetrastannanes[4] have been prepared, and germacyclobutanes are well-known.[1b] The direct and preparatively useful access to the 1,3-di-Grignard reagent of propane (**2a**)[5] and of its 2,2-dimethyl derivative **2b**[6] from the corresponding dibromides opens a new approach to metallacyclobutanes. We here report the synthesis of 1,1-dimethylstannacyclobutane (**1a**) and 1,1,3,3-tetramethylstannacyclobutane (**1b**).

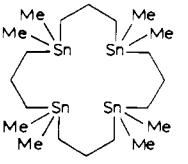
When a stoichiometric amount of dichlorodimethylstannane (**3**) was added to **2a** at room temperature and the reaction mixture was hydrolyzed and subjected to GC-MS, none of the expected **1a** but only its cyclic oligomers **4a** (dimer), **5a** (trimer), and **6a** (tetramer), formed in about 70% total yield, could be observed.



4a



5a



6a

Although **1a** had also been formed, it escaped direct observation with the exception of a singlet in the ^{1}H NMR spectrum when the reaction was performed in dioxane-d_8 (δ 0.39, $^{2}J_{SnH}$ = 52, 54 Hz); due to its characteristic low-field position (cf. **1b**), this signal must be assigned to the methyl groups of **1a**. Attempts to isolate **1a** were thwarted by its high volatility, which prevented its separation from the ether, and by its instability, as it did not survive the conditions of GC-MS. Compelling evidence for the presence of **1a** was obtained when the reaction mixture was subjected to distillation at room temperature under reduced pressure. The distillate was treated with a ca. 10-fold excess of **2a**, followed by H_2O (or D_2O) to give **7**[7] (or **7**-d_2, respectively, Scheme I). Under

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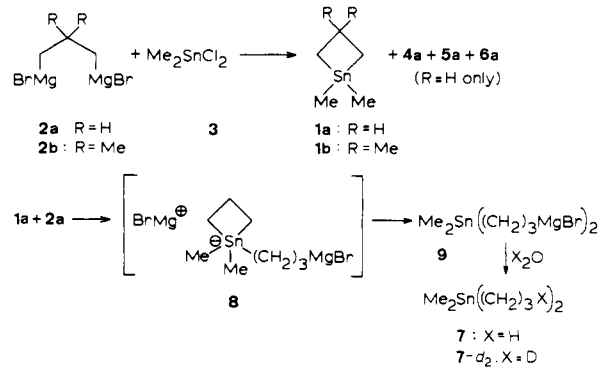
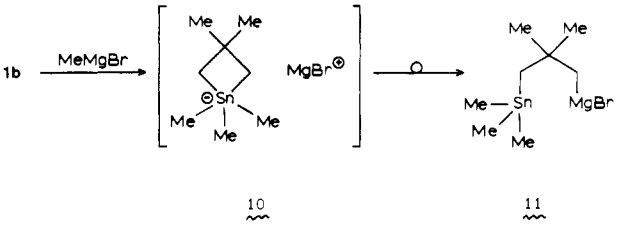
Scheme I



Scheme II



these conditions, **4a**, **5a**, and **6a** are not volatile; moreover, they are inert toward **2a**. Therefore, the formation of **7** can be explained only by the reaction of **1a** with **2a**; via the intermediate ate complex **8** the di-Grignard reagent **9** is formed, which with D_2O gives **7**-d_2. An analogous ring opening of 1,3-distannacyclobutanes with methyllithium has been observed by Seyferth and Lefferts.[3b]

More success was achieved in our efforts to directly identify and isolate **1b**, the 3,3-dimethyl derivative of **1a**. It was formed in 48% yield in the stoichiometric reaction of **2b** with **3** in diethyl ether (Scheme I). The yield was determined as follows: after 0.5 h at 25 °C, the volatile compounds were distilled in vacuo from the reaction mixture into a solution of methylmagnesium bromide in diethyl ether; presumably, **1b** reacted via the ate complex **10** to give **11** (Scheme II), which on hydrolysis gave (trimethylstannyl)neopentane (**12**), independently synthesized from neopentylmagnesium bromide and chlorotrimethylstannane; deuterolysis of **11** gave **12**-d_1.

The isolation of **1b** was achieved in the following way. First, the diethyl ether was removed from **2b** by addition of the high-boiling polyether bis(2-*n*-butoxyethoxy)methane and distillation of all low-boiling material in vacuo (a similar treatment of **2a** would lead to considerable decomposition due to β-hydride elimination[5]). To the remaining solution, **3** was added at room temperature, and after 0.5 h, **1b** was distilled in vacuo out of the reaction mixture into a liquid nitrogen trap. A colorless liquid of practically pure **1b** was thus obtained (5% isolated yield) and characterized by its spectral data.[8]

The properties of **1b** convincingly demonstrate its monomeric structure. Typical is its high volatility, in contrast to that of **4a**, and the fact that its molecular ion can be observed in the mass spectrum on electron impact ionization (70 eV), though with low intensity (1%). All other cyclic dimethyltin compounds reported here showed no detectable molecular ion under this condition, the highest mass ions observed being $[M - CH_3]^+$ or even smaller fragment ions. We believe this to be a consequence of the rapid cleavage of an endocyclic Sn-C bond in $\mathbf{1b}^{+\cdot}$ under relief of ring strain; the structure of the observed ion is therefore probably $Me_2{}^+SnCH_2CH_2CH_2{}^{\cdot}$.

Similarly unique and characteristic are the ^1H and ^{13}C NMR resonances of the 1-methyl groups of **1b**. They occur at much lower field (in dioxane-d_8: δ (^1H) 0.39 ($^2J_{SnH}$ = 53.1, 55.6 Hz); δ (^{13}C) 15.4) than those of the strain-free oligomers in $CDCl_3$: (**4a**) δ (^1H) 0.02 ($^2J_{SnH}$ = 48-50 Hz); δ (^{13}C) -11.8. Qualitatively, these low-field shifts can be understood as a consequence of the presumably rather small CH_2-Sn-CH_2 bond angle, imposed by the geometry of the four-membered ring. This increases the p character of the endocyclic bonds of the tin atom and in turn the s character and thus the electronegativity in its exocyclic bonds toward the methyl groups. The increased values of $^2J_{SnH}$ for the methyl groups of **1b** may also reflect this effect.

In view of the reported instability of stannacyclopentanes,[2] it was not surprising that **1b** was not stable at room temperature. With air, it reacted immediately under formation of a white precipitate of unknown composition (cf. the slow reaction of stannacyclopentanes with oxygen[2]). In solution **1a** and **1b** polymerized; **4-6** were not formed from **1**. The rate of polymerization of **1b** was strongly solvent dependent: at room temperature, $t_{1/2} \approx 30$ days in toluene-d_8 while in ethereal solvents such as dioxane-d_8, $t_{1/2} \approx 2$ days. Preliminary NMR results suggest that in the latter case, the solvent is also consumed to a certain extent, which indicates its active participation in the polymerization process.

Registry No. 1a, 85443-02-3; **1b**, 85443-03-4; **2a**, 62934-64-9; **2b**, 83528-98-7; **3**, 753-73-1; **4a**, 85443-04-5; **5a**, 85443-05-6; **6a**, 85443-06-7; **7**, 56535-52-5; **7**-d_2, 85443-07-8; **9**, 85452-92-2; **11**, 85443-08-9; **12**, 55204-72-3; **12**-d_1, 85443-09-0; MeMgBr, 75-16-1.

(7) **7**: ^1H NMR (90 MHz, $CDCl_3$) δ 0.00 (s, $^2J_{SnH}$ = 49.0, 51.0 Hz, 6 H, SnMe), 0.82 (t, $^3J_{HH}$ = 8.0 Hz, $^2J_{SnH} \simeq$ 50 Hz, 4 H, $SnCH_2$), 1.04 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, Me), 1.35-1.75 (m, 4 H, CH_2CH_2Me); mass spectrum, *m/z* 236 (1) [$M^{+\cdot}$, calcd for $C_8H_{20}Sn$ 236.0586, obsd 236.0589], 221 (6) [M - Me]$^+$, 193 (75), 151 (100).

(8) **1b**: ^1H NMR (90 MHz, dioxane-d_8) δ 0.39 (s, $^2J_{SnH}$ = 53.1, 55.6 Hz, 6 H, SnMe), 1.13 (s, 6 H, CMe), 1.54 (s, $^2J_{SnH}$ = 52 Hz, 4 H, CH_2); ^1H NMR (250 MHz, toluene-d_8) δ 0.25 (s, $^2J_{SnH}$ = 54 Hz, 6 H, SnMe), 1.25 (s, 6 H, CMe), 1.65 (s, $^2J_{SnH}$ = 52 Hz, 4 H, CH_2); ^{13}C NMR (62.89 MHz, dioxane-d_8) δ 15.4 (q, $^1J_{CH}$ = 126 Hz, SnMe), 34.5 (t, $^1J_{CH}$ = 125 Hz, $SnCH_2$), 35.6 (q, $^1J_{CH}$ = 125 Hz, C*Me*), 40.3 (s, *C*Me); ^{13}C NMR (62.89 MHz, toluene-d_8) δ -6.5 (q, $^1J_{CH}$ = 129 Hz, SnMe), 34.0 (t, $^1J_{CH}$ = 132 Hz, $SnCH_2$), 35.6 (q, $^1J_{CH}$ = 132 Hz, C*Me*), 40.2 (s, *C*Me); mass spectrum, *m/z* 220 (1) [$M^{+\cdot}$, calcd for $C_7H_{16}Sn$ 220.0273, obsd 220.0263], 205 (6) [M - Me]$^+$, 150 (61), 135 (100).

Oxygenation of Chloroalkenes by Superoxide in Aprotic Media

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Although primary and secondary haloalkanes are readily oxidized by superoxide ion (O_2^-) in aprotic media via an S_N2 mechanism,[1-4] simple alkenes are unreactive.[5-7] In a recent study of polychloro hydrocarbons,[8] we observed that chloroethene and trichloroethene also did not react at significant rates with O_2^- in dimethyl sulfoxide. However, we now report that *cis*-1,2-dichloroethene, trichloroethene, and tetrachloroethene among others are rapidly oxygenated by O_2^- in dimethylformamide (DMF) or acetonitrile.

The extent of the reaction of electrogenerated O_2^- with chloroalkenes has been determined by cyclic voltammetry of O_2 in the presence of excess substrate.[8] The overall reaction and product stoichiometries for the degradation of the chloroalkene substrates

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