

Whereas the diastereomeric pair (**4d/5d**) was still clearly distinguishable in the <sup>1</sup>H-NMR spectrum (see Table 1), in the case of (**8d/9d**) a nuclear resonance spectroscopic assignment was no longer possible. The selectivity achieved was less than 1.5% *ee*, as shown by a comparison of the specific rotations of the liberated alcohols (**10d/11d**) and the reference compound (**10d/11d**)<sup>[12]</sup> prepared from the enriched 2-phenylpropanediol **12** (*S*:*R* = 3.3:1  $\cong$  54% *ee*). The ratio of (**8c/9c**) determined by 250-MHz <sup>1</sup>H-NMR<sup>[13]</sup> (1.1:1  $\cong$  5.0% *de*) was also significantly lower than that of the corresponding oxymethylene diastereomers (**4c/5c**).<sup>[14]</sup>

With the experiments presented here it could be shown that an asymmetric induction with predictable direction (even with slightly decreasing selectivity with increasing chain length) is possible via an oxymethylene structure. If one considers the reaction from the formal aspect of a 1,*n*-asymmetric induction then the ratio 2:1 ( $\cong$  33% *de*) found experimentally for (**4d/5d**) is so far the highest value known to us for a 1,10-asymmetric induction. From the point of view of a naturally related system of chiral compounds,<sup>[3]</sup> based on stereoelectronic effects, the direction of the reaction effected by a left helix corresponds fundamentally to that which is induced by an acetal group of the B family (configuration like  $\alpha$ -L-glucose or  $\beta$ -D-glucose). Consequently, there is also a correlation of  $\alpha$ -D-glucose (acetalic center of the A-type) with a dextrorotatory oxymethylene helix.

The actual occurrence of oxymethylene structures in the presence of silicates under potentially prebiotic conditions together with the predictable specificity of the enantiomerically pure helix make it seem possible that optically active paraformaldehyde has played a role in the amplification (perpetuity) of chirality in the course of chemical evolution.

### Experimental

The compounds **2** to **5** (in each case **b**, **c**, **d**) were characterized <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopically and by elemental analyses. For data and experimental details not mentioned in this communication see: P. Etmayer, *Diplomarbeit*, Technische Universität Wien 1987. The compounds **6** to **11** (each **c** and **d** were characterized <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopically).

Reaction with methylmagnesium iodide: A 0.705 M solution of MeMgI (5.4 mL, 3.82 mmol) was diluted with 5 mL of ether, cooled, and treated with 0.636 mmol of ketone **3** in 10 mL of anhydrous ether. After 20 min the mixture was diluted with 10 mL of petroleum ether and extracted with 20 mL of 10% NH<sub>4</sub>Cl solution. The organic phase was washed once with NaHCO<sub>3</sub>, dried, and evaporated to dryness.

Reaction with methylmagnesium iodide and zinc chloride: A solution of ketone **3** (0.636 mmol) in anhydrous ether (10 mL) was cooled to 0°C and treated with a solution of ZnCl<sub>2</sub> (150 mg, 1.1 mmol) in anhydrous ether (10 mL). After 15 min the cloudy solution was added in bulk to a solution of 5.4 mL (3.82 mmol) of a 0.705 M MeMgI solution and 5 mL of anhydrous ether cooled to -40°C. After 20 min the heterogeneous reaction solution was diluted with 30 mL of petroleum ether and extracted with 20 mL of 10% NH<sub>4</sub>Cl solution. The organic phase was washed once with saturated NaHCO<sub>3</sub> solution, dried, and evaporated to dryness.

Reaction with methyllithium: The reaction was carried out in ether analogously to the reaction with methylmagnesium iodide.

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[5] 35.8% **2a**, 19.0% **2b**, 6.9% **2c**, 4.3% **2d**, and 11.5% **1a** were obtained. For further experimental data and <sup>13</sup>C-NMR and <sup>1</sup>H-NMR spectra of **2a** see Ref. [3].  
[6] **3a** could be obtained in 70% **3b** in 72%, **3c** in 66%, and **3d** in 66% yield. According to 90-MHz <sup>1</sup>H-NMR and 22.5-MHz <sup>13</sup>C-NMR all the products are pure compounds at room temperature.  
[7] a) The absolute configuration of (**4a/5a**) could be determined via the specific rotation of the alcohol described in the literature [7b], which was obtained from (**4a/5a**) by methanolysis (cleavage of the protecting group **1a** under acid conditions in methanol); b) see E. L. Eliel, J. P. Freeman, *J. Am. Chem. Soc.* 74 (1952) 23.  
[8] We assume that one of the free electron pairs on the acetal oxygen is stabilized exo-anomerically with the  $\sigma^*$  orbital of the C-O bond in the ring and that the aryl ketone is so arranged that a further anomeric stabilization by n- $\sigma^*$  interaction of the second electron pair on the oxygen with the  $\sigma^*$  orbital of the C-CO-aryl bonding is possible. We obtained evidence for this conformation by an X-ray structure analysis of compound **2a**.  
[9] [2*R*-(2 $\alpha$ (*R*\*),3 $\alpha\alpha$ ,4 $\alpha$ ,7 $\alpha$ ,7 $\alpha\alpha$ )]-2-[(Octahydro-7,8,8-trimethyl-4,7-methanobenzofuran-2-yl)oxy]-1-phenylbutan-1-one.  
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[11] The compounds **6c** and **6e** were synthesized analogously to the procedure given in the literature: D. J. Pasto, K. Garves, M. P. Serve, *J. Org. Chem.* 32 (1967) 774.  
[12]  $[\alpha]_{D}^{20} = 18.5$  ( $c = 3.5$ , ether) based on 100% *ee*.  
[13] Selected <sup>1</sup>H-NMR data for diffraction of the diastereomeric pairs **8c/9c**: **8c**,  $\delta = 3.979$  (d,  $J = 7.3$  Hz, 1H, 7aH), **9c**,  $\delta = 3.968$  (d,  $J = 7.3$  Hz; 1H, 7aH) (NMR spectra: Bruker Spectrospin, 250 MHz, CDCl<sub>3</sub>, 20°C, referred to TMS).  
[14] The specific rotation,  $[\alpha]_{D}^{20} = -1.4$  ( $c = 2.6$ , ether) based on 100% *ee*, was too low for an informative comparison.

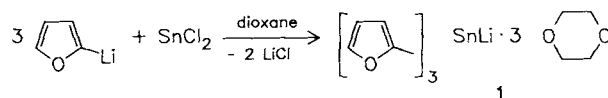
## Solid State Structure of a Lithium Triorganostannate

By Michael Veith,\* Cornelius Ruloff, Volker Huch, and Fritz Töllner

Dedicated to Professor Hans Bock on the occasion of his 60th birthday

Lithium triorganostannates have been used for several years for the transfer of triorganostannyl groups to electrophilic centers.<sup>[1,2]</sup> Although there is no lack of methods for their synthesis,<sup>[3]</sup> all attempts to determine their structures directly have thus far failed because the compounds were neither isolable nor crystallizable. Especially regarding mechanistic problems there are controversial discussions as to whether, e.g., the lithium atom is bound to the tin atom or an ion pair is present,<sup>[3]</sup> or when these different structures must be reckoned with. In continuation of our studies in the area of metal alkoxystannates,<sup>[4]</sup> we have now succeeded in preparing lithium tris( $\alpha$ -furyl)stannate **1** as the first compound of this kind in crystalline form and in investigating it by X-ray structure analysis.

For the synthesis of **1** we used  $\alpha$ -furyllithium<sup>[5]</sup> and tin(II) chloride. The colorless crystalline platelets of **1** obtained as precipitate formally contain three dioxane molecules per lithium atom.



The dioxane molecules are bound with different strengths. Two of these molecules can be cleaved from the

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compound (elemental analysis of the remaining product) under reduced pressure and at slightly elevated temperature ( $10^{-3}$  torr,  $50^{\circ}\text{C}$ ). The chemical shifts and the coupling constants of the hydrogen atoms of the furyl moiety of **1** and the characteristics of the unit cell of **1** are collected in Table 1.

Table 1. Some  $^1\text{H-NMR}$ , crystal, and structural parameters of **1**.

|   |
|---|
| $\text{C}_{48}\text{H}_{66}\text{Li}_2\text{O}_{18}\text{Sn}_2$ , $M_r = 1182.29 \text{ g mol}^{-1}$  |
| $^1\text{H NMR}$ (furyl region only, $[\text{D}_2]\text{acetoneitrile}$ ):  |
| $\delta = 6.25$ (dd, $J(\text{H}_b, \text{H}_c) = 1.6 \text{ Hz}$ , 1H, $-\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{O}$ ),   |
| $6.33$ (d, $J(\text{H}_a, \text{H}_b) = 2.9 \text{ Hz}$ , 1H, $-\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{O}$ ),   |
| $7.71$ (d, $J(\text{H}_a, \text{H}_c) = 0.5 \text{ Hz}$ , 1H, $-\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{O}$ )  |
| Triclinic space group: $P\bar{1}$ , $a = 1089(1)$ , $b = 1372(1)$ , $c = 1974(3) \text{ pm}$ ,  |
| $\alpha = 102.5(1)$ , $\beta = 104.6(1)$ , $\gamma = 91.25(8)^{\circ}$ , $V = 2775 \times 10^6 \text{ pm}^3$ , $Z = 2$ , 7037 reflections in the range $3^{\circ} < 2\theta < 50^{\circ}$ , 2603 classified as "not observed" ( $F_0 < 4\sigma(F_0)$ ), 445 parameters. $R = 0.073$ , $R_w = 0.084$ |

Figure 1 shows a drawing of the centrosymmetric anion of **1** based on the results of the X-ray structure analysis.<sup>[6]</sup> It follows therefrom that compound **1** is not to be formulated as a simple tris(furyl)lithium stannate, but as an ion

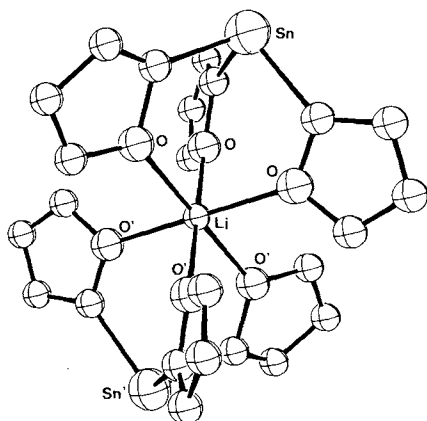
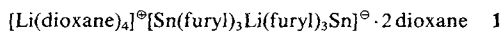


Fig. 1. Structure of the anion  $\{[\text{Sn}(\text{furyl})_3\text{Li}(\text{furyl})_3\text{Sn}]^{\ominus}\}$  of **1**. The unmarked atoms are C atoms. The following Li–O distances are found in the cation  $[\text{Li}(\text{dioxane})_4]^{\oplus}$ : 186(3), 193(3), 193(3) and 194(3) pm. Some averaged bond lengths [pm] and angles [ $^{\circ}$ ] in the anion: Sn–C 218.8(9), Li–O<sub>eq</sub> 209.6(9), Li–O<sub>ax</sub> 229(1), C<sub>α</sub>–C<sub>β</sub> 136(1), C<sub>β</sub>–C<sub>γ</sub> 141(1), C<sub>γ</sub>–C<sub>δ</sub> 131(1), C<sub>α</sub>–O 141(1), C<sub>δ</sub>–O 138(1); C–Sn–C 96(2), O–Li–O 87–93.

pair consisting of a lithium ion coordinated by four dioxane units and a complex anion. The anion is formally formed by reaction of a lithium ion with two tris(furyl)stannate ions. Two crystallographically independent but structurally very similar anions are located with their inversion centers at the positions 0,0,0 and 0,0,0.5 of the unit cell, while the cation assumes a general position. Two further dioxane molecules are accommodated in the crystal without interacting with metal atoms; hence, the following general formula can be given for the crystalline compound **1**:



The tin atoms have the typical pyramidal geometry for threefold coordinated tin(II) atoms,<sup>[7]</sup> with C–Sn–C angles of approximately  $90^{\circ}$ . The lithium atom in the cation  $[\text{Li}(\text{dioxane})_4]^{\oplus}$  has almost ideal tetrahedral coordination, whereas in the anion it is coordinated by a distorted octahedral array of oxygen atoms from the furyl groups. Four

"equatorial" Li–O distances (mean value 209.6(9) pm) can easily be differentiated from the "two axial" distances (229(1) pm), so that the coordination geometry around the lithium atom can also be described as square planar with additional axial interaction. We attribute the observed distortion about the lithium atom in the anion of **1** not to electronic but to steric effects: on the one hand, lithium atoms normally strive for tetrahedral coordination (with an expected Li–O value of 190–195 pm)<sup>[8]</sup> and, on the other, the mutual distance of the oxygen atoms is predetermined by the specific geometry in the tris(furyl)stannate ions. The only possible alternative would appear to be the compromise found in the given structure.

### Experimental

A suspension of  $\text{SnCl}_2$  (1.26 g, 6.6 mol) in  $\text{Et}_2\text{O}$  (40 mL) was treated rapidly at  $-50^{\circ}\text{C}$  with a solution of furyllithium (20 mmol) **5** in  $\text{Et}_2\text{O}$  (50 mL). After warming to room temperature the mixture was stirred for 8 h and filtered (to remove LiCl). After separation of volatile components by condensation there remained pale yellow crystals, which were recrystallized from 30 mL of dioxane; **1** forms colorless platelets. Yield: 1.76 g (45%).

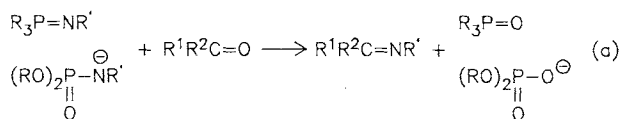
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### A Novel Entry to the PC-Double Bond: the "Phospha-Wittig" Reaction

By *Angela Marinetti* and *François Mathey\**

The archetypal Wittig and Wittig-Horner olefinations of carbonyl compounds have less popular equivalents in nitrogen chemistry<sup>[1]</sup> [Eqn. (a)]. We therefore wondered



whether it would be possible to extend this kind of chemistry [Eqn. (a)] to phosphorus. In practice, this meant that it was necessary to have a ready and general access to phosphorus species such as **1** or **2**.



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