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Tetraacylstannanes as Long-Wavelength Visible-Light Photoinitiators with Intriguing Low Toxicity

Judith Radebner,[a] Anna Eibel,[b] Mario Leypold,[a] Nina Jungwirth,[a] Thomas Pickl,[a] Ana Torvisco,[a] Roland Fischer,[a] Urs Karl Fischer,[c] Norbert Moszner,[c] Georg Gescheidt,[b] Harald Stueger,[a] and Michael Haas*[a]

Abstract: The first tetraacylstannanes Sn[(CO)R]₄ (R = 2,4,6-trimethylphenyl (1a) and 2,6-dimethylphenyl (1b), a class of highly efficient Sn-based photoinitiators, were synthesized. The formation of these derivatives was confirmed by NMR spectroscopy, mass spectrometry, and X-ray crystallography. The UV/Vis absorption spectra of 1a, b reveal a significant redshift of the longest wavelength absorption compared to the corresponding germanium compounds. In contrast to the known toxicity of organotin derivatives, the AMES test and cytotoxicity studies reveal intriguing low toxicity. The excellent performance of 1 as photoinitiators is demonstrated by photobleaching (UV/Vis) and NMR/CIDNP investigations, as well as photo-DSC studies.

From the Bronze Age (3500 BC) onward, tin has been a highly appreciated metal and raw material for further processing. Its acquisition marks an important part in the evolution of mankind. Pioneering works in organometallic tin chemistry by Frankland,[16] Cadet,[2] or Zeise[3] sparked the interest into organotin derivatives. Advances in analytical techniques, including Sn NMR, X-ray diffraction, or appropriate computational methods aided organotin chemistry to be a thriving field of research. Besides being used as fungicides, insecticides or stabilizers in polyvinyl chloride (PVC), organostannanes are widely used in chemical synthesis. However, due to the acute toxicity of organotin compounds, their use in synthetic chemistry has been connoted quite negatively and gradually diminished recently.

Tetraacylstannanes 1a, b as a unique class of long-wavelength visible-light PIs for free-radical photopolymerization. Tetraacylstannanes 1a, b are accessible in a remarkably easy-to-perform one-pot reaction (Scheme 1). Notably, this new PI system shows very low cytotoxicity (XTT₅₀ value of 108.53 μg/mL), in line with its low water solubility.[18] Moreover, the bacterial reverse-mutation test, the so-called Ames test, proved that 1 does not induce gene mutations, which is remarkable for organotin compounds.[18] Structurally related acylgermanes show similar low cytotoxicity (e.g., benzoyltrimethylgermane: XTT₅₀

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and Sn or Ge compounds. Additionally, photo-products of P-based PI s are known to be highly toxic.[23] In this context, acylgermanes and acylstannanes are promising PIs for applications requiring biocompatibility.

Recently, our group published a series of papers on previously unknown acylgermanes.[12,24–26] Exploiting the multiple silyl abstraction enabled the targeted synthesis of these highly efficient PIs in high yields. Moreover, the strength of this reaction sequence lies in its high functional-group tolerance.[24,25]

Following the results obtained for tetraacylgermanes, we discovered that the reaction of potassium stannide 2K[27] with 4.1 molar equivalent of acid fluoride F–(CO)R (R = aryl) leads to the formation of tetraacylstannanes 1. Mechanistically speaking, 2K undergoes a salt metathesis reaction with the respective acid fluoride, in which KF and tris(trimethylsilyl)acylstannane 3 are formed.

The consecutive nucleophilic attack of the fluoride ion on 4, originating from the formation of 2K, in situ generates Me3SiF 5 and tBuO–, which further reacts with 3 to form the stannenolate 6. Accordingly, 4 and 5 could be detected by NMR spectroscopy in the reaction mixture (δ[29Si] = 30.3 and 6.92 ppm, respectively).[28] Subsequently, the applied excess of acid fluoride immediately reacts with 6 to the respective bisacylstannane 7 releasing again KF and 4. Acylation proceeds until all trimethylsilyl groups are abstracted, and the final product 1 is formed (Scheme 2). It appears that di-ortho substitution at the phenyl ring is necessary for the successful preparation of tetraacylstannanes. To date, no derivatives with a different substitution pattern were isolated. We assume that the di-ortho substitution prevents the nucleophilic attack of any reactive anionic intermedium formed (F– or tBuO–). A characteristic feature of tetraacylstannanes 1 is the 11C NMR resonance for the carbonyl group, which appears between 243 and 244 ppm. A similar tendency was found for tetraacylgermanes and -silanes.[6,16]

The analytical data for 1a and b (see the Supporting Information) are consistent with the proposed structures. As a representative example, the structure of 1a is depicted in Figure 1. The structural features of these tin derivatives corre-

![Image of Scheme 1](image1)

**Scheme 1.** Synthesis of tetraacylstannanes 1a and b.

![Image of Scheme 2](image2)

**Scheme 2.** Proposed mechanism for the synthesis of tetraacylstannanes.

**Figure 1.** ORTEP representation of 1a. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] with estimated standard deviations: Sn(1)–C(1) 2.244(2), Sn(1)–C(11) 2.247(2), Sn(1)–C(21) 2.247(2), Sn(1)–C(31) 2.256(2), C–O (mean) 1.208; C–Ge–C (mean) 111.7; O–C–Cp(1)–Cp(2) (mean) 70.5.

215 µg mL⁻¹.[6,14] In contrast, for the widely applied phosphorus-based PIs (e.g., Irgacure 819) any reports on cytotoxic and AMES tests are available.[12,20] However, a similar acylphosphine oxide[21] was reported to show a higher cytotoxic (XTT) toxicity than Sn or Ge compounds. Additionally, photo-products of P-based PIs are known to be highly toxic.[23] In this context, acylgermanes and acylstannanes are promising PIs for applications requiring biocompatibility.

![Image of Figure 2](image3)

**Figure 2.** UV/Vis absorption spectra of 1a, b and 2a, b (the respective germainium-analogues) and 3 (bisacylphosphine oxide Irgacure 819; chloroform solution, c = 10⁻⁵ mol L⁻¹).
gest-wavelength absorption bands, which were computationally assigned to the HOMO–LUMO transition and show considerable charge-transfer character. Upon excitation, electron density is displaced from the n(C=O)/s(Sn–C) bonding HOMO to the π*(C=O/Aryl) antibonding LUMO (Figure 3), which results in the population of an orbital with antibonding character between the Sn–C bond.

In comparison to the respective germanium analogues 2a and b and to bisacylphosphine oxide 3 (Scheme 3), the extinction coefficient of 1a and b are significantly increased. The bathochromic shifted λ_{max} as well as the increased extinction coefficient, induce a more pronounced tailing into the visible-light region >450 nm, enabling α-cleavage upon irradiation with light sources operating >450 nm. Hence, 1 represents a radical source with most promising absorption properties for visible-light applications (Table 1).

To assess the efficiency of 1a and b as radical photoinitiators, we have performed photobleaching experiments. Steady-state photolysis (SSP) upon irradiation with an LED operated at 470 nm reveals remarkably fast bleaching of 1a and b compared to germanium- and phosphorus-based photoinitiators 2 and 3 (Figure 4). Fast photobleaching of the initiator is an indication for efficient radical formation and is moreover crucial for achieving high curing depths and colorless polymers.[31] Compound 1b exhibits the fastest photobleaching, whereas bisacylphosphine oxide 3 shows almost no bleaching, being unsuitable for curing applications in this wavelength region. The superior photobleaching performance of tetracylstannanes 1 over the reference initiators 2 and 3 upon irradiation with high wavelength visible light (470 nm) is consistent with the bathochromically shifted absorption spectra (Figure 2).

We have investigated the radical reaction pathways upon irradiation of 1a and b in presence of monomers by using chemically induced dynamic nuclear polarization (CIDNP) NMR spectroscopy. This method allows following the α-cleavage of the photoinitiators 1a and b and provides information about reaction products formed through radical pairs (Sn/C; Scheme 4). Radical-pair-based phenomena lead to enhanced absorptive or emissive NMR signals of reaction products, caused by a non-Boltzmann population of magnetic energy levels.[5, 23] Figure 5 compares the 1H NMR and CIDNP spectra of 1a recorded in presence of butyl acrylate BA (see the Supporting Information for the corresponding spectra of 1b). Polarized signals of the hydrogen atoms of the parent compound (at δ = 2.25 ppm (1), δ = 6.67 ppm (2), and δ = 1.99 ppm (3)) can

| Table 1. Experimental and PCM(CHCl3) TD-DFT CAM-B3LYP/LANL2DZ-dp-ECP(Sn),def2-TZVP(H,C,O)//B3LYP/LANL2DZ-dp-ECP(Sn),6-31+G(d)(H,C,O) calculated wavelength absorption maxima, λ [nm], extinction coefficients ε [dm³ mol⁻¹ cm⁻¹], and oscillator strengths f for 1a and b (CHCl3). |
|-----------------|-----------------|-----------------|-----------------|
|                | λ_{max}, exp. [Å] | λ_{max}, calc. [Å] | Absorption edge | Assignment               |
| 1a             | 398 (1776)       | 416, 409, 389 (0.0221, 0.0051, 0.0137) | 480             | n(n-π*) (CO/Aryl)        |
| 1b             | 396 (1735)       | 414, 407, 389 (0.0167, 0.0053, 0.0131) | 480             | n(n-π*) (CO/Aryl)        |

Figure 3. HOMO (left) and LUMO (right) of mesityloytrimethylstannane, a simplified version of 1a, to illustrate the Frontier orbitals of tetracylstannanes 1a and b.

Figure 4. a) Photobleaching of 1a upon irradiation at 470 nm. b) Plots of normalized absorbance versus time for compounds 1a, b, 2a, and 3, monitored at absorption maxima (1a 398 nm; 1b 396.5 nm; 2a 375 nm; 3 369.5 nm; 3 409 nm). Samples: 0.6 mM PI in acetonitrile.

Scheme 3. Reference Compounds: Tetracylgermanes 2a, b and bisacylphosphine oxide 3.

Scheme 4. α-Cleavage of tetracylstannane derivatives 1a and b, leading to the formation of a tin-centered radical Sn and a benzoyl-type radical B.
be attributed to the (cage) re-formation of 1a, indicating a partly reversible α-cleavage. The characteristic singlet at δ = 10.5 ppm appearing in enhanced absorption corresponds to the aldehyde proton of the benzaldehyde derivative BH, clearly indicating α-cleavage of 1a (Scheme 4 and Figure 5). Analogous signals have been observed in the CIDNP spectra of several photoinitiating systems containing a benzoyl moiety.[32] The formation of BH is attributed to a disproportionation reaction (β-hydrogen transfer) between a benzoyl-type radical and radicals, which are able to donate hydrogen atoms (growing polymer chain).[32,33] Figure 5 additionally shows a strongly polarized emissive multiplet at δ = 4.49 ppm and an absorptive multiplet at δ = 3.37 ppm. These signals are tentatively assigned to the methylene protons of species SnBAB, which is formed upon addition of benzoyl radical B to a chain radical initiated by Sn (Figure 5). The analogous photoproduct has been observed for tetraacylgermanes.[5] We assume that rotation around the C–C bond derived from BA (marked in pink in the structure of SnBAB, Figure 5) is sterically hindered by the adjacent bulky mesitoyl group, making the signal at δ = 4.49 ppm appear as a doublet of doublets, instead of a triplet.

The prepared compounds were also investigated by means of photo-DSC measurements to get fast and accurate information on their initiation efficiency. With a single photo-DSC measurement, various significant parameters are accessible. From the height of the exothermic peak, the rate of polymerization $R_p$ (mol L$^{-1}$ s$^{-1}$) can be calculated. The overall heat evolved ($\Delta H_p$) gives information on the final double conversion (DBC). Furthermore, the time to reach the maximum heat flow ($t_{\text{max}}$) can be derived from the photo-DSC plots. Herein, the photocuring of the crosslinking monomer 1,6-hexandiol diacrylate (HDDA) with 1a was investigated ($t_{\text{max}}$ ≈ 4.5 s, $R_{\text{p, max}}$ > 0.31 mol L$^{-1}$ s$^{-1}$, DBC ≈ 59%). The previously reported tetraallylgermane 2a was used as reference compound, showing comparable reactivity to 1a under the chosen experimental condi-

**Figure 5.** $^1$H NMR and CIDNP spectra of 1a (10 mM solution in [D$_3$]acetone-t$_{1}$), recorded in the presence of butyl acrylate monomer (BA, 50 mM).

**Figure 6.** Photo-DSC (a) and conversion plots (b) for the photopolymerization of HDDA with 0.3 w% photoinitiator. Samples were stabilized with 1000 ppm BHT prior to the measurement to prevent spontaneous polymerization. Photo-DSC and conversion plots are depicted in Figure 6. A summary of the DSC parameters can be found in the Supporting Information.

In summary, we could synthesize and fully characterize the first examples of tetraaclylstannanes, representing a class of highly efficient VL PIs. Unprecedently, the found photochemical properties are beneficial over those known for Ge- or P-based PIs. Additionally, the low toxicity gives rise to any application, in which biocompatibility and costs are an issue. SSP experiments show that the tetraaclylstannanes 1a and b are promising initiators for high-wavelength visible-light curing. CIDNP experiments confirm α-cleavage of 1a and b and efficient addition of tin-centered radicals and benzoyl radicals to monomer double bonds. High activity as photoinitiator was further verified by photo-DSC experiments.

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**Conflict of interest**

The authors declare no conflict of interest.

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[1] E. von Frankland, *Ann. Chem. Pharm.* 1849, 71, 171.
[2] D. Seyferth, *Organoanetetics* 2003, 14, 1488.
[3] W. C. Zeise, *Ann. Phys. Chem.* 1831, 97, 497.
[4] a) G. J. D. Peddle, *J. Organomet. Chem.* 1968, 14, 139; b) A. Cappuccini, A. Degl’Innocenti, C. Faggi, G. Reginato, A. Ricci, *J. Org. Chem.* 1989, 54, 2966; c) M. Kosugi, H. Naka, H. Sano, T. Migitani, *Bull. Chem. Soc. Jpn.* 1987, 60, 3462.
[5] D. Neschadim, A. Rossepointner, M. Griesser, B. Lang, S. Mosquera-Vazquez, E. Vauthey, V. Gorelk, R. Liska, C. Hametner, B. Ganster, R. Saf, N. Moszner, G. Gescheidt, *J. Am. Chem. Soc.* 2013, 135, 17314.
[6] J. Radebner, A. Eibef, M. Leypold, C. Gersche, L. Schuh, R. Fischer, A. Torvisco, D. Neschadim, R. Geier, N. Moszner, R. Liska, G. Gescheidt, M. Haas, H. Stueger, *Angew. Chem. Int. Ed.* 2017, 56, 3103; *Angew. Chem.* 2017, 129, 3150.
