



Prof. Armido Studer

Curriculum Vitae

Born: 24. 2. 1967
Marital Status: married
Nationality: Swiss

Elementary and High School

- 1974 – 1982 Elementary School in Visperterminen (1974-1980) and Visp (1980-1982).
- 1982 – 1987 High School in Brig (Kollegium Spiritus Sanctus).
- Final examination in May 1987 (Matura Type C).

University Career

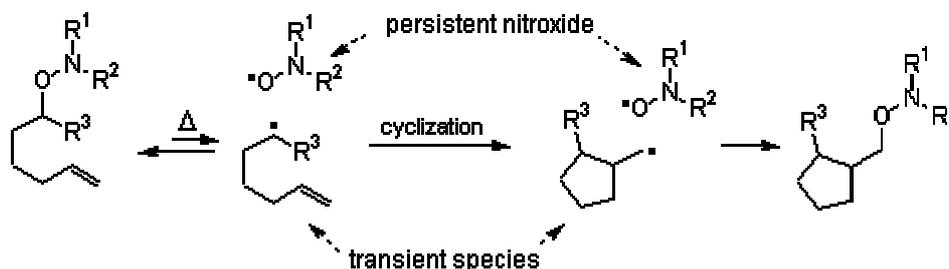
- 1987 – 1991 Studies in chemistry at the ETH in Zürich. Diploma thesis in the research group of Prof. Dr. D. Seebach (Synthesis of Novel Tripeptides).
- 1992 – 1995 PhD. student at the ETH in Zürich under the guidance of Prof. Dr. D. Seebach (New Applications of 2-*tert*-Butylimidazolidinones in Asymmetric Synthesis).

- **1995 – 1996** Postdoctoral Fellow of the Swiss National Science Foundation at the University of Pittsburgh (USA) in the group of Prof. Dr. D. P. Curran.
- **1996 – 2000** Independent research on the development of new synthetic methods in the field of free radical chemistry. "Habilitation" at the Laboratory of Organic Chemistry, ETH Zürich (October 2000).
- **2000 – 2004** Associate Professor of Organic Chemistry at the Philipps-University of Marburg, Germany.
- **since April 2004** Full Professor of Organic Chemistry at the Westfälische Wilhelms-Universität of Münster, Germany.

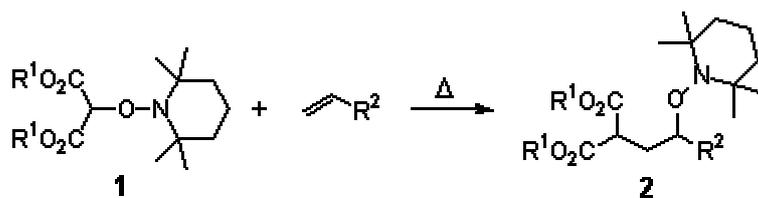
Research Interests

[Tin-Free Radical Reactions Using the Persistent Radical Effect](#)

The Persistent Radical Effect (PRE) is a general principle that explains the highly specific formation of the cross-coupling product between two radicals. When one species is persistent (long lived) and the other transient the two radicals are formed at equal rates. The initial buildup in concentration of the persistent species, caused by the self-termination of the transient radical, steers the reaction subsequently to follow a single pathway the cross reaction. We have used the PRE for the conduction of environmentally benign radical cyclization reactions. Nitroxides are generally used as persistent radicals in these processes.



New nitroxides have been designed and have been tested in radical isomerization reactions. Alkoxy-amines of type **1**, which are readily prepared from commercially available starting materials, undergo thermal additions to various nonactivated double bonds to provide γ -functionalized malonates **2**, which are synthetically highly useful building blocks. The addition reactions can be combined with radical cyclization and fragmentation processes.



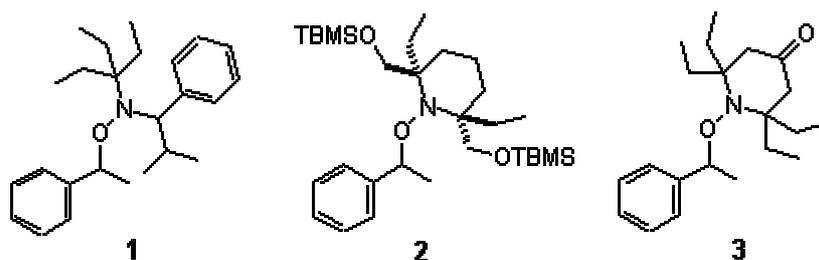
Moreover, we have shown that the PRE-mediated processes can efficiently be performed under microwave irradiation. The reactions can be conducted in less than 10 minutes in high yields. In addition, difficult radical cyclizations, which cannot be performed under classical heating, can be conducted under microwave irradiation.

It is important to note that we are also interested in physical organic aspects of this chemistry. For example, the kinetics of the various processes involved in the PRE-mediated radical reactions are investigated using state of the art techniques. For example, kinetic EPR-experiments are used to determine the C-O-bond energies of the various new alkoxyamines studied. Along with the kinetics, the dynamic processes are simulated using *PowerSim*, a program for modelling nonlinear dynamic processes.

[Controlled Radical Polymerizations - Chemical Modification of Surfaces and Nanotubes](#)

Well-defined polymers with polydispersities below the theoretical limit for a conventional radical polymerization (1.5) can nowadays be prepared by living free radical polymerization. Nitroxide-mediated polymerizations (NMP), atom transfer radical polymerizations (ATRP) and RAFT polymerizations belong to this category. The control of the polymerization in the NMP is based on the reversible formation of a dormant alkoxyamine from the corresponding nitroxide and the chain growing polymer radical (see also PRE). The concentration of free radicals remains low during the entire polymerization, thus ensuring a very low fraction of irreversible termination via polymer radical dimerization/disproportionation.

During the last four years we have introduced several new alkoxyamines for the controlled NMP of styrene and of *n*-butyl acrylate. For example, alkoxyamines **1**, **2** and **3** which are readily prepared are highly efficient initiators/regulators for the controlled polymerization of acrylates. In fact, alkoxyamine **3** is the best regulator known to date and Di- and Tri-block copolymers with narrow polydispersities can be prepared using this alkoxyamine.

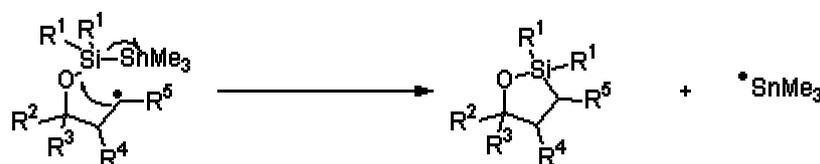


The polymerization studies performed are always accompanied with kinetic studies. The activation energy for the C-O-bond homolysis of each new alkoxyamine initiator is determined using EPR spectroscopy. Moreover, alkoxyamine stabilities are measured using NMR spectroscopy. These careful physical studies allow us to design even better alkoxyamines.

Using the novel alkoxyamines, we are currently preparing complex polymer architectures (block- and graft-copolymers). Moreover, smart polymers are under investigation. The "grafting from" approach is used for the preparation of polymer brushes. Properties of the surface can be adjusted. This kind of process will also be used for the chemical modification of the inner as well as of outer surface of nanotubes. The chemically modified surfaces are analyzed using state of the art techniques such as FT-ATR-IR, multi angle light scattering, and AFM.

[Intramolecular Homolytic Substitution Reactions at Silicon](#)

Despite the tremendous achievements in free radical chemistry during the last two decades, many basic transformations still remain to be discovered in this field. Certainly, S_{H2} reactions at heteroatoms belong to this category. Intramolecular S_{H2} type reactions at group XIV elements have not been studied in depth. We have recently introduced a new highly interesting radical approach to cyclic alkoxy silanes by intramolecular homolytic substitution (S_{HI}) at silicon.

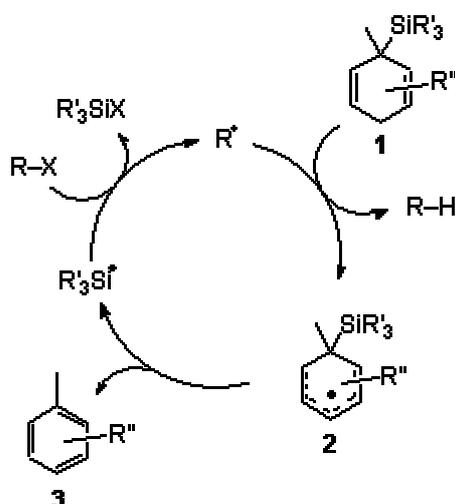


We showed that the homolytic substitution works well for alkyl and aryl radicals. More recently the same reaction has successfully been conducted with acyl radicals providing cyclic acyl silanes. Moreover, the method can also be applied for the stereocontrolled formation of highly substituted cyclic vinyl silanes. Currently, the mechanism of the S_{HI} reaction at silicon is under

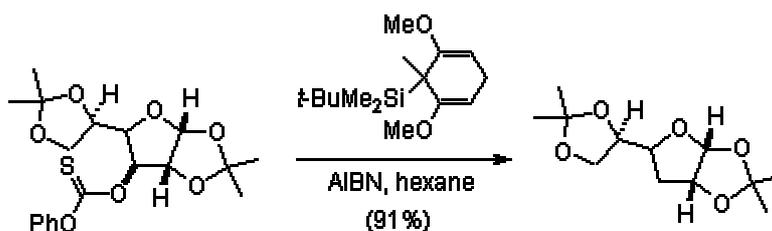
investigation. Homolytic substitutions at silicon are important in the oxidative degradation of polysilanes which are important materials.

Functionalized Cyclohexadienes in Radical Reactions

We recently introduced readily prepared silylated 1,4-cyclohexadienes of type **1** as new radical reducing agents, which can replace the toxic tin hydrides in various radical reactions such as dehalogenations, deselenations, deoxygenations, cyclizations, and intermolecular radical addition reactions.



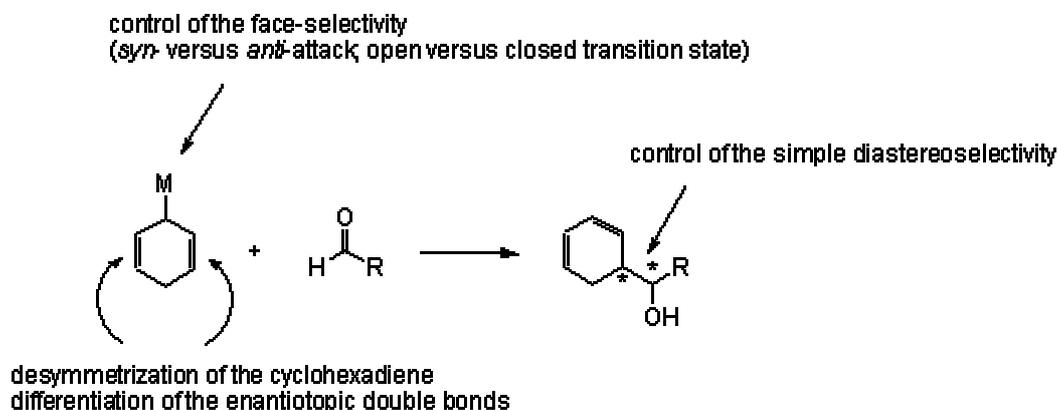
The cyclohexadiene bis-allylic CH_2 -moiety acts as the H-donor in these chain reactions. Reduction of a radical R with a reagent of type **1** affords cyclohexadienyl radical **2**. Rearomatization of **2** then provides the corresponding silyl radical, which is able to propagate the chain by reaction with a starting halide, xanthate or phenylselenide R-X . Arene **3** is formed as the byproduct. In these cleverly designed reagents, rearomatization is the driving force for the expulsion of the chain propagating silyl radicals. As example, a radical deoxygenation using a phenyl thionocarbonate ester with one of our new reagents is presented below. The new reagents have already been applied by others in *complex natural product synthesis*. These reagents are currently probably the *best alternative* to the toxic tin hydrides for the conduction of reductive radical chain reactions. Furthermore, these reagents can also be used for the hydrosilylation of non-activated double bonds in a process called the "*transfer-hydrosilylation*".



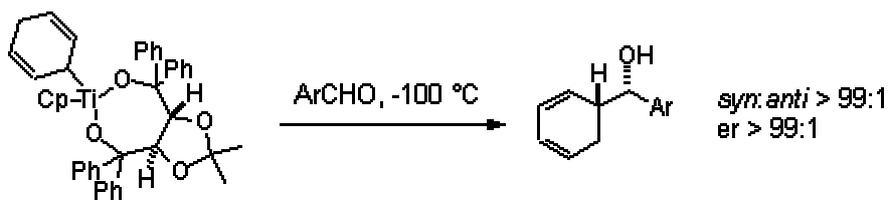
In collaboration with John Walton the rearomatization process (**2**→**3**) has been carefully studied using EPR spectroscopy. Functionalized 1,4-cyclohexadienes are highly useful precursors for the generation of various heteroatom centered radicals. We are currently investigating several other functionalized 1,4-cyclohexadienes which can be used for radical reactions

Ionic Reactions using Functionalized Cyclohexadienes

Recently, metalated cyclohexadienes have been used as nucleophiles in stereoselective ionic reactions. The stereoselective addition of such metalated dienes to aldehydes is a highly challenging process. Several issues have to be considered for a successful stereocontrol. The most difficult task is certainly the desymmetrization of the diene.



We found that upon using chiral cyclohexadienyl Ti-compounds the diastereoselectivity and also the enantioselectivity can be controlled. In the reaction with aromatic aldehydes excellent diastereo- and enantioselectivity was obtained. The chiral product dienes are highly useful building blocks for further synthetic manipulations.



The new method was first applied for the synthesis of (+)-nephrosteranic acid. In just five steps (+)-nephrosteranic acid was prepared starting from commercially available 1,4-cyclohexadiene in a good overall yield. The same approach has meanwhile been used for the synthesis of (+)-*trans*-whisky lactone and (+)-*trans*-cognac lactone. Currently, we are studying catalytic versions of the above described desymmetrization reaction. Moreover, the method will be applied for the synthesis of other natural products.