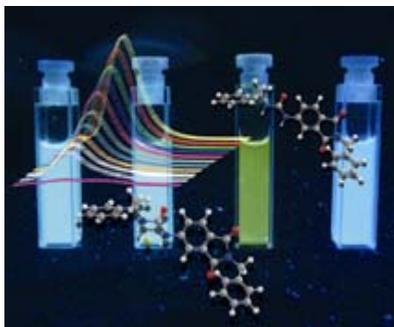


**Honda-Fujishima Award 2009  
to the  
Griesbeck Photochemistry Group**

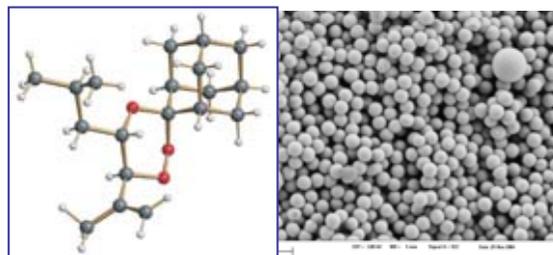


Our research group is active in synthetic and mechanistic photochemistry, mainly in:

- **Photooxygenation and Photocatalysis**

We are using different oxygen species such as *triplet oxygen* ("type I photooxygenations"), singlet oxygen in "type II photooxygenations", and the *superoxide* radical anion in photo electron transfer initiated (PET) reactions ("type III photooxygenations"). These reactions can be useful for the activation of several substrate classes such as electron-rich or radicalophilic alkenes, dienes or alkynes, enones and  $\alpha,\beta$ -unsaturated carboxylic acid derivatives. By use of non-conjugated, aryl-substituted dienes it is possible to design bicyclization reactions

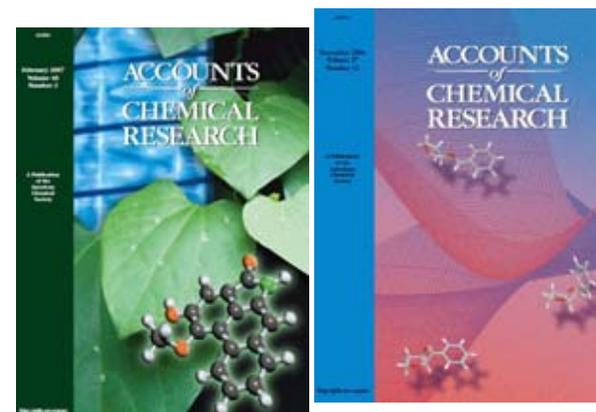
with subsequent oxygen trapping in order to synthesize bicyclic endoperoxides and by a singlet oxygen approach also 1,2,4-trioxanes. This research has found actual applications in the synthesis of potential anti-Malaria compounds which are structurally related to artemisinin (*qinghaosu*), the antimalarial active component from a plant extract used in China for over 2000 years. These projects are performed in collaboration with the faculty of medicine and several Institutes for tropical medicine.



- **Photoinduced Electron Transfer**

In the course of our investigations of phthalimide photochemistry we discovered a surprisingly efficient activation of omega-amino carboxylic acids, i.e. the macrocyclization of these compounds by way of PET decarboxylation and biradical combination. High dilution conditions which normally are the essential prerequisite for these C-C bond forming

reactions are not necessary here. We propose ground-state chelation effects to be responsible for this phenomenon and currently try to strengthen this assumption by NMR, IR, UV and X-ray crystallographic methods. Recent applications are the syntheses of benzodiazepines, benzoazepinediones (medium ring sizes) as well as the synthesis of cyclopeptides and cyclic amines and lactames with ring sizes  $>24$ .

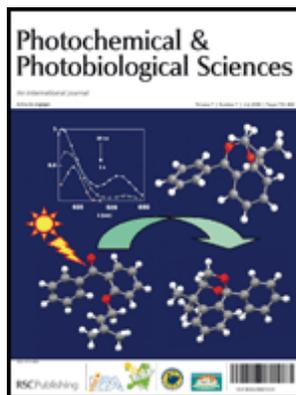


- **Organic Spin-Photochemistry**

The factors determining the stereochemical course of triplet photocycloaddition reactions are still a matter of debate. For understanding the configuration of the products resulting from triplet reactions, the knowledge of the geometries where the molecule crosses from the triplet to the  $S_0$  surface

is essential. It is expected, that there is a structural dependency between selectivity and spin-orbit coupling (SOC) elements which are responsible for the spin inversion process in these tight 1,4-triplet biradical geometries. Our principal objective is to elaborate these structural factors by investigating the effect of substrate variations, temperature effects, radical clocks, and heavy atom effects on the diastereoselectivity of Paternò-Büchi and de Mayo reactions. Especially interesting (and still quite dubious) are cycloaddition reactions with aromatic substrates which in some cases proceed with extremely high regio- and diastereoselectivity. In order to learn more about the contribution of ground state conformations *versus* SOC geometries we have also started to calculate energies and SOC values by means of *ab initio* methods. We are also studying the results of magnetic isotope effects on the stereoselectivity of photochemical reactions, a real *terra incognita*.

### International Relationships:



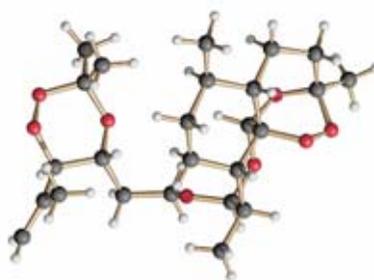
European Photochemistry Association,  
European Society for Photobiology,  
International Union of Pure and Applied Chemistry (Titular Member)

### Cooperations

France, Austria, USA, Japan, Taiwan, Spain, Italy, Crete, Switzerland, Croatia

### Contact

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Viktor **Schlundt**, Russia  
Sarah **Strohmeier**  
Johannes **Uhlig**  
Elmar **Zimmermann**

### Recent publications:

*Acc. Chem. Res.* **2007**, *40*, 128.  
*Org. Lett.* **2007**, *9*, 611.  
*Angew. Chem. Int. Ed.* **2007**, *46*, 8883.  
*Photochem. Photobiol. Sci.* **2008**, *7*, 782.  
*Austr. J. Chem.* **2008**, *61*, 573-580.  
*Adv. Syn. & Cat.* **2008**, *350*, 2104.  
*Organic Letters* **2008**, *10*, 3965.  
*Molecules* **2008**, *13*, 1745.  
*Tetrahedron Lett.* **2009**, *50*, 121.  
*Tetrahedron* **2009**, *65*, 1438.  
*Synlett* **2009**, 1514.  
*J. Med. Chem.* **2009**, *52*, 3420.