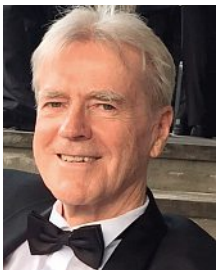
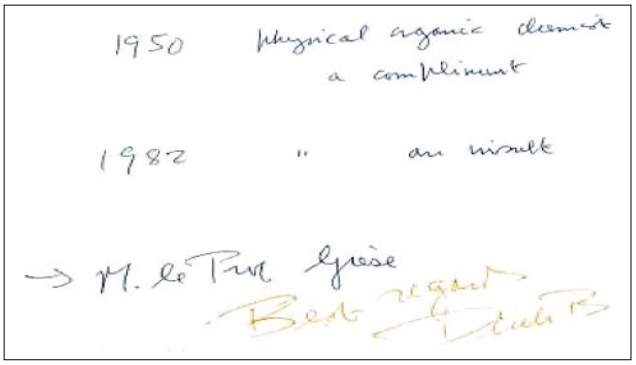
Editorial

Physical Organic Chemistry



Bernd Giese

This year, 2016, two journals of Chemical Societies, the *Israel Journal of Chemistry* and *CHIMIA*, are publishing special issues on Physical Organic Chemistry. What does that mean? A 'friendly' thanks and good-bye? That was the feeling in the early 1980s. After a long, blooming period of physical organic chemistry the synthetic organic community sighed, "give me a break". The situation was deliberately characterized by Derek Barton after a discussion at an EUCHEM conference on synthetic organic chemistry, where he handed me a note saying:[1]



Let's check this annotation, one generation later. This CHIMIA issue is a good litmus test. I had asked colleagues who are working or got their PhD in Switzerland to contribute to a special issue on Physical Organic Chemistry. And the result is: three out of seven articles are highlighting the close link between physical and synthetic organic chemistry. Eric Meggers shows how the understanding of chain reactions of radicals and radical cations can be the basis for catalytic, asymmetric syntheses. His goal is the development of "new innovative strategies for achieving cooperative asymmetric photoredox catalysis". Christian Bochet makes clear that "in comparison with their thermal counterpart, photochemical reactions have been much less explored, and there is little doubt that a deeper understanding of their mechanisms, together with their use as key steps in the synthesis of complex molecules will gradually dissipate the common misconception of unpredictability and bring back essentially atom-economical processes into the limelight". Thomas Bally describes that in "electrocyclic reactions of radical cations ...the rules we have learned to apply to corresponding neutral reactions do not apply, and are replaced by other factors, the most important of which is often vibronic coupling to low-lying excited states". That is, these three articles are examples for the fact that one can use reactive intermediates like radicals, radical cations and biradicals for synthesis only if one understands the physical organic effects in the ground and excited state.

Often, these reactive intermediates are generated by electron transfer reactions, and Oliver Wenger explains the surprising statement that "theory predicts a regime in which electron transfer rates *in*crease with increasing distance between reactands", and the first experimental example has just appeared in *Angew. Chem*.[2] Armido Studer describes a "method for the detection of ... transient radicals (which) are important in organic chemistry, polymer chemistry, biology and medicine". He uses "verdazyl radicals as ... spin sensors, ... which undergo transformation from paramagnetic non-fluorescent state to a diamagnetic fluorescent state".

Two articles deal with chemical and biochemical reactions that do not involve reactive intermediates. Marcel Mayor shows in his tutorial on the mathematical description of atropisomerization that "dynamic behaviour is a fascinating property of natural and artificial systems and (how) its understanding has a significant impact to transform interchanges into controlled molecular motion". Andreas Marx builds the bridge to molecular biology. "For DNA replication, repair and recombination ... enzymes have to unscramble the code and recognize the complementary nucleotide out of a pool of four structurally similar deoxynucleotide triphosphates ... This review highlights the mechanistic basis for selecting the right nucleotide by DNA polymerases."

I sincerely thank my colleagues and friends who contributed to this issue. It was a great pleasure for me to edit this issue, and I wish you the same thrill reading the articles.

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[1] B. Giese, *Isr. J. Chem*. **2016**, *56*, 91.
[2] M. Kuss-Petermann, O. S. Wenger, *Angew. Chem. Int Ed.* **2016**, *55*, 815.

The Editorial Board of CHIMIA expresses its thanks to the Guest Editor Prof. Bernd Giese for organizing this special issue on 'Physical Organic Chemistry', admirably demonstrating that this topic is as interesting and relevant as it ever was.