cyklus Innovation Lectures (INNOLEC)

IC066 The structure and chemistry of reactive intermediates

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posluchárna **K8M309**, pavilion A8 (kampus Bohunice)

A. Survey of Some Short-Lived Species. Their Structures, Methods for Generation, Typical Chemical Reactions and Theoretical Considerations.

References: (a) Anslyn, E. V.; Dougherty D. A. . *Modern Physical Organic Chemistry* University Science, Sausalito, CA **2006.** (b) Moss, R. A.; Platz, M. S.; Jones. M.; *Reactive Intermediate Chemistry* Wiley, Hoboken, NJ **2004.**

B. Selected Case Studies from the Classic and Recent Literature:

1. **Carbenium Ions.** References: (a) Winstein, S. Klindinst, P. R.; Robinson, G.C. "salt Effects and Ion Pairs in Solvolysis and Related Reactions." *J. Am. Chem.. Soc.* **1961,** *83*, 885. (b) "Dynamic Processes Leading to Covalent Bond Formation for Sn1 Reaction" K. S. Peters, *Acc. Chem. Res.* **2007**, *40*, 1-7.

2. **Nitrenes.** References (a) "Kinetics, Spectroscopy and Computational Chemistry of Arylnitrenes" N. P. Gritsan and M. S. Platz *Chemical Review*, **2006**, *106*, 3844-3867. (b) Warmuth, R. Makowlek, S. "The Phenylnitrene Rearrangement in the Inner Phase of a Hemicarcerand" *J. Am. Chem. Soc.* **2005**, *127*, 1084.

3. **Nitrenium Ions.** References: (a) Heller, H. E.; Hughes, E.D. Ingold, C.K. "A New View of the Hydroxylamine Rearrangement" *Nature* **1951**, *168*, 909. (b) Miller, J.A. "Cacinogenesis by Chemicals: An Overview" *Cancer Res.* **1970**, *30*, 559. (c) Novak, M.; Rajagopal, S. "N-Arylnitrenium Ions" *Adv. Phys. Org. Chem,* **2001**, *136,* 167.

4. **Diradicals.** References: (a) : Bekele, T.; Christian, C. F.; Lipton, M. A.; Singleton, D. A. "Concerted" transition state, stepwise mechanism. dynamics effects in (C2-C6) enyne allene cyclizations " *J. Am. Chem Soc.* **2005**, *127*, 9216=9223. (b) Pedersen, S. Herek, J. L.; Zewail, A. H. "The Validity Of The Diradical Hypothesis - Direct Femtosecond Studies Of The Transition-State Structures" *Science*, **1994**, *266*, 1359-1364. (c) Baldwin, J. E.; Andrist, A. H.; Pinschmirk, "Orbital Symmetry Disallowed Energetically Concerted Reactions" *Acc. Chem. Res.* **1972**, *5*, 402.

5. **Benzynes.** References: (a) "Reactive 1,4-Dehydroaromatics" R. G. Bergman, *Acc. Chem. Res.* **1973**, *6*, 25-31. (b) Sander, W. "m-Benzyne and p-Benzyne" *Acc. Chem. Res.* **1999**.*32*, 669-676.. (c) Wolkernberg S. E. Boger, D. L. "Mechanisms of in situ activation for DNA-targeting antitumor agents" *Chem. Rev.* **2002**, *102*, 2477-2495.

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