Reactive Organophosphorus Species: Synthesis, Structure, and Reactivity

Mardyukov, A.,[1]* Schreiner, P. R.[1]
*presenter
[1] atur.mardyukov@org.chemie.uni-giessen.de. Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany.

Phosphinidenes (R–P:) are a class of reactive intermediates, which are of considerable importance in a variety of organic reactions.[1] Due to their high reactivity, the chemical properties of phosphinidenes have been deduced almost exclusively from trapping or complexation experiments.[2] The talk reports the first synthesis, IR, and UV/Vis spectroscopic characterization of parent phenylphosphinidene (**1**) and its reactions with small molecules (**2-4**). As products of these reactions, we have been able to identify a series of elusive intermediates using matrix isolation spectroscopy (Figure 1).[3-4] We illustrate that the chemical transformations involved are distinctly different from those observed with triplet nitrenes.

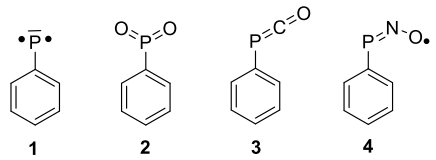

Figure 1.

Moreover, the first spectroscopic (IR and UV/Vis) characterization of (4-methoxy)phenyl phosphine disulphide (**5**) and phenyl phosphine diselenide (**6**) together with their unexplored photochemistry will be presented (Figure 2).[5-6] These hitherto unreported molecules have been postulated as key intermediates derived from Lawesson's and Woollins' reagents that are extremely useful in sulfur and selenium transfer reactions. We also isolated higher congeners of nitroso- and thionitrosobenzene, namely phenylphosphinide oxide (**7**) and phenylphosphinidene sulphide (**8**) using a combination of photolysis, matrix-isolation IR, and UV/Vis spectroscopic methods as well as quantum-chemical computations.[7]

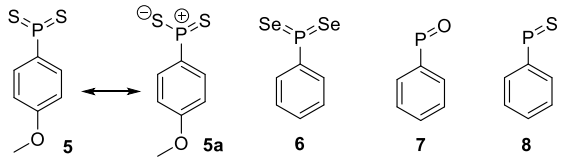

Figure 2.

[1]Aktas, H.; Slootweg, J. C.; Lammertsma, K., Nucleophilic Phosphinidene Complexes: Access and Applicability. *Angew. Chem., Int. Ed.* **2010,** *49* (12), 2102-2113. [2]Shah, S.; Simpson, M. C.; Smith, R. C.; Protasiewicz, J. D., Three Different Fates for Phosphinidenes Generated by Photocleavage of Phospha-Wittig Reagents ArP:PMe3. *J. Am. Chem. Soc.* **2001,** *123* (28), 6925-6926. [3]Mardyukov, A.; Niedek, D., Photochemical reactions of triplet phenylphosphinidene with carbon monoxide and nitric oxide. *Chem. Commun.* **2018,** *54* (97), 13694-13697. [4] Mardyukov, A.; Niedek, D.; Schreiner, P. R., Preparation and Characterization of Parent Phenylphosphinidene and Its Oxidation to Phenyldioxophosphorane: The Elusive Phosphorus Analogue of Nitrobenzene. *J. Am. Chem. Soc.* **2017,** *139* (14), 5019-5022. [5]Mardyukov, A.; Keul, F.; Schreiner, P. R., Preparation and Characterization of Phenyl Phosphine Diselenide - The Monomeric Form of Woollins' Reagent. *Eur. J. Org. Chem.* **2019**, 387-390. [6]Mardyukov, A.; Niedek, D.; Schreiner, P. R., Unravelling Lawesson's reagent: the structure of monomeric (4-methoxyphenyl)phosphine disulfide. *Chem. Commun.* **2018,** *54* (22), 2715-2718. [7]Mardyukov, A.; Keul, F.; Schreiner, P. R., Isolation and Characterization of the Free Phenylphosphinidene Chalcogenides $C_6H_5P{=}O$ and $C_6H_5P{=}S$, the Phosphorous Analogues of Nitrosobenzene and Thionitrosobenzene. *Angew. Chem., Int. Ed.* **2020,** *59* (30), 12445-12449.