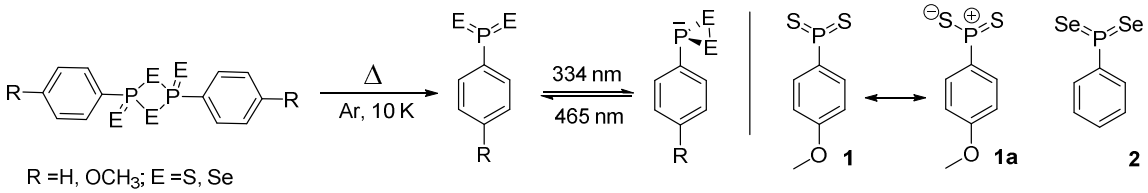
Preparation and Characterization of Species with Molecular Formula RPE_2: The Monomeric Forms of Lawesson's and Woollins' Reagents

Artur Mardyukov,[a] Peter R. Schreiner[a]*

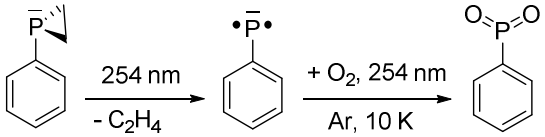
[a]*Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany, artur.mardyukov@org.chemie.uni-giessen.de*

Compounds of type RPE_2 (R = alkyl, aryl; E = O, S, Se) present unusual bonding, namely a tri-coordinated phosphorus atom in the formal oxidation state of +5; this makes such compounds highly electrophilic at phosphorus and they typically self-aggregate to form linear or cyclic compounds.[1-3] However, evidence for the existence of RPE_2 species is scarce and indirect as it comes from a trapping experiment. To avoid self-aggregation two main routes have been used: (i) stabilization of the monomer with bulky substituents[4,5] and (ii) using Lewis bases, e.g., pyridine or *N*-heterocyclic carbenes (NHCs) that coordinate to the electrophilic phosphorus atom.[6,7]



R =H, OCH_3; E =S, Se

The talk reports, the first synthesis, IR, and UV-Vis spectroscopic characterization of the (4-methoxy)phenyl phosphine disulphide (**1**) and phenyl phosphine diselenide (**2**) together with their unexplored photochemistry (Scheme 1).[8,9] These hitherto unreported molecules have been postulated as the key intermediates derived from Lawesson's and Woollins' reagents (**2**) that are extremely useful in sulfur and selenium transfer reactions. The computational and vibrational analysis suggests no identification of ylide type resonance form for **1**, and the structure of **1** is best depicted as two nearly equal P=S double bonds.[8] Moreover, the synthesis of the previously elusive phenyldioxophosphorane (the phosphorus analogue of nitrobenzene, $PhPO_2$; **4**) under matrix isolation conditions by the reaction of triplet phenylphosphinidene (**3**) with triplet molecular oxygen (^3P-O_2) will be also discussed (Scheme 2).[10]



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