

N°931 / PC

TOPIC(s) : Homogenous, heterogenous and biocatalysis

## Advances in Catalytic Wittig-Type Reactions based on P(III)/P(V) Redox Cycling

### AUTHORS

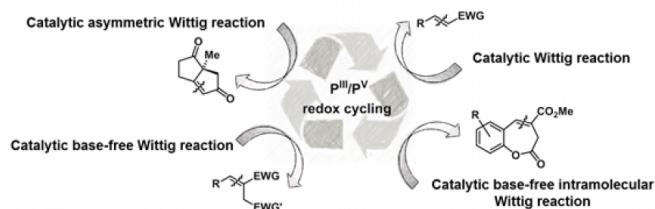
Thomas WERNER / LEIBNIZ INSTITUTE FOR CATALYSIS, ALBERT-EINSTEIN-STR. 29A, ROSTOCK

Lars LONGWITZ / LEIBNIZ INSTITUTE FOR CATALYSIS, ALBERT-EINSTEIN-STR. 29A, ROSTOCK

### PURPOSE OF THE ABSTRACT

Numerous organic transformations are based on phosphorus reagents. For instance, in the Wittig reaction which is probably the most recognized method for the chemo- and regioselective olefination of carbonyl groups phosphorus ylids are employed. In this reaction stoichiometric amounts of phosphane oxide are formed as by-products, which often significantly hamper the product purification. Recently, progress in the development of transformations based on P(III)/P(V) redox cycling e.g. catalytic Wittig reactions has been made.[1] In this respect, we developed catalytic Wittig reactions[2] based on commercially available phosphanes and  $\alpha$ -oxides, a microwave-assisted variant of this method[3] as well as the first example of an enantioselective catalytic Wittig reaction.[4] Herein, we present our studies on the development of base-free catalytic variant of the Wittig reaction.[5] The addition of simple Brønsted acids as co-catalysts for the in situ reduction of the formed phosphane oxide significantly facilitates the conversion.[6] This allows performing the reactions under milder conditions and with higher efficiency. Based on these findings we developed an intramolecular variant of the base-free catalytic Wittig reaction using a phospholene oxide as pre-catalyst which gives facile access to benzoxepinones derivatives.[7]

## FIGURES



**FIGURE 1**

Selected transformations based on  $P(III)/P(V)$  redox cycling

**FIGURE 2**

## KEYWORDS

Wittig reaction | homogeneous catalysis |  $P(III)/P(V)$  redox cycling | olefination reaction

## BIBLIOGRAPHY

- [1] a) Z. Lao, P. H. Toy, *Beilstein J. Org. Chem.* 2016, 12, 2577; b) L. Longwitz, T. Werner, *Pure Appl. Chem.* 2019, 91, 95.
- [2] T. Werner, M. Hoffmann, S. Deshmukh, *Eur. J. Org. Chem.* 2015, 3286.
- [3] M. Hoffmann, S. Deshmukh, T. Werner, *Eur. J. Org. Chem.* 2015, 4532.
- [4] T. Werner, M. Hoffmann, S. Deshmukh, *Eur. J. Org. Chem.* 2014, 6630.
- [5] M.-L. Schirmer, S. Adomeit, A. Spannenberg, T. Werner, *Chem. Eur. J.* 2016, 22, 2458.
- [6] M.-L. Schirmer, S. Jopp, J. Holz, A. Spannenberg, T. Werner, *Adv. Synth. Catal.* 2016, 358, 26.
- [7] A. Grandane, L. Longwitz, C. Roolf, A. Spannenberg, H. Murua Escobar, C. Junghanss, E. Suna, T. Werner, *J. Org. Chem.* 2019, 84, 1320.