

# SYNLETT Spotlight 457

## 6-Diphenylphosphinopyridin-2-(1H)-one (6-DPPon)

Compiled by Vahid Khakyzadeh



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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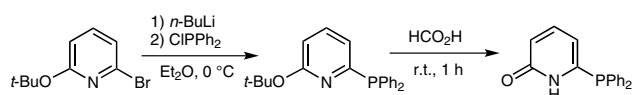
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Dedicated with best wishes to Prof. Dr. Bernhard Breit at Albert-Ludwigs-Universität Freiburg

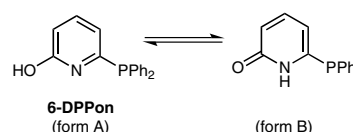
### Introduction

Among heterocyclic structural units, pyridines are the most prevalent and have attracted the attention of chemists.<sup>1</sup> One important aspect of pyridine chemistry is designing new ligands based on the pyridine core.<sup>2</sup> Inspired by DNA base pairing, 6-DPPon (white solid, mp: 187 °C) was introduced by Bernhard Breit (Albert-Ludwigs-Universität Freiburg) as a monodentate ligand.<sup>3</sup> This compound can not only be easily prepared (Scheme 1) but also has a brilliant property: the ability for self-assembly.<sup>4</sup>



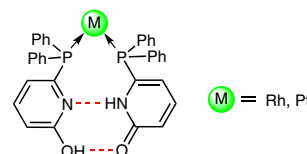
**Scheme 1** Preparation of 6-DPPon

6-DPPon has two tautomeric forms, a 2-pyridone and a 2-hydroxypyridine tautomer (Scheme 2).



**Scheme 2** Tautomeric forms of 6-DPPon

Interaction between form A and form B through hydrogen bonding can in situ generate a bidentate donor ligand in the coordination sphere of a metal (rhodium and platinum) center (Scheme 3). The present subject can open new gates to the design of self-assembled ligands and can be considered in related chemistries.

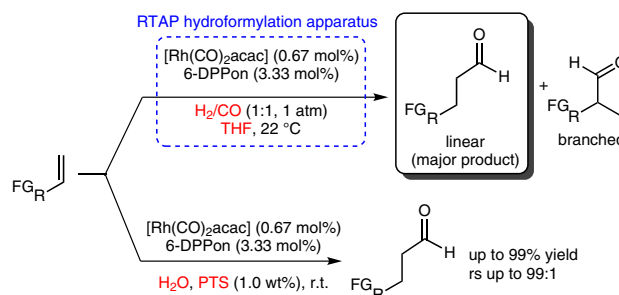


**Scheme 3** Self-assembly of the 6-DPPon ligand

### Abstracts

#### (A) Room Temperature Ambient Pressure (RTAP) Hydroformylation of Terminal Alkenes

Breit and co-workers have developed a hydroformylation of terminal alkenes under mild conditions: at room temperature and under ambient pressure. A bidentate donor ligand, generated in situ by self-assembly of 6-DPPon, reacted with rhodium and created a new catalyst with unique properties. Various ligands were tested in comparison to 6-DPPon and the best results (high yield and little isomerization) were obtained with 6-DPPon. High selectivity, low catalyst loading, a high level of generality, and excellent reactivity were some promising aspects of this protocol.<sup>5</sup> It was found that terminal alkenes can be hydroformylated in aqueous media by slightly changing the reaction conditions. Breit and co-workers investigated various surfactants, and the results indicated that polyoxyethanyl- $\alpha$ -tocopheryl sebacate (PTS) was the best choice. Interestingly, 6-DPPon was the best ligand for this reaction. It is worth noting that in addition to the advantages described above, with the new protocol the structure of the self-assembly catalyst is stable in water as a protic solvent; an important point for self-assembled structures.<sup>6</sup>



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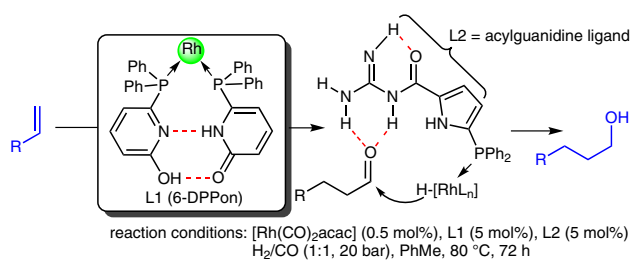
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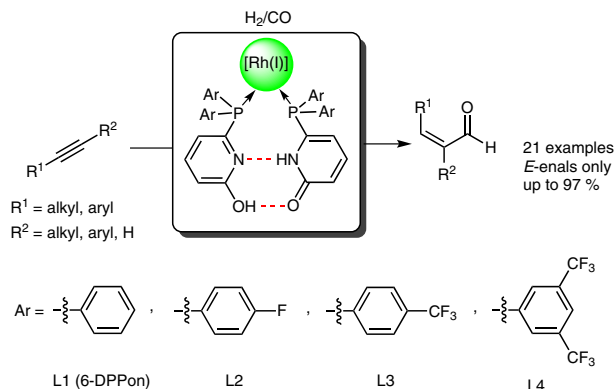
## (B) Tandem Rhodium-Catalyzed Hydroformylation–Hydrogenation of Alkenes

In 2012, a unique tandem reaction was designed. In this reaction, a one-pot conversion of alkenes into linear alcohols is achieved using two different transformations (hydroformylation of alkenes and aldehyde hydrogenation). The first step (hydroformylation) was mediated by a rhodium complex which was generated by coordination of two 6-DPPon's, and a second step was carried out with an acylguanidine ligand. High regioselectivity and simultaneous a highly chemoselective reduction were two highlights of this work.<sup>7</sup>



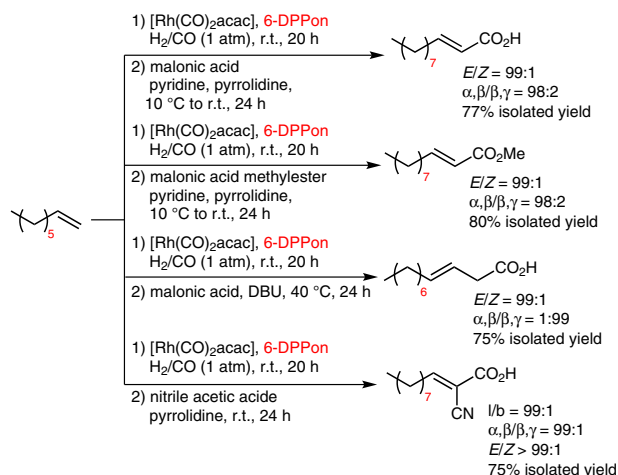
## (C) Hydroformylation of Alkynes

Alkynes were hydroformylated stereo- and chemoselectively using 6-DPPon as a self-assembling ligand. In this study, several derivatives of the mentioned ligand were designed and investigated. This was the first time that dialkyl- as well as diaryl-substituted alkynes furnished *E*-enals with excellent chemo- and stereoselectivity.<sup>8</sup>



## (D) One-Pot C3-Homologation of Terminal Alkenes

A new method to furnish carbonyl and carboxylic compounds was established by Breit and co-workers. In this method, by a combination of regioselective RTAP hydroformylation with 6-DPPon and a rhodium catalyst followed by decarboxylative Knoevenagel reaction (organocatalysis), various interesting compounds were produced.<sup>9</sup> In all of the reactions, the presence of 6-DPPon was crucial.



## References

- Bull, J. A.; Mousseau, J. J.; Pelletier, G.; Charette, A. B. *Chem. Rev.* **2012**, *112*, 2642.
- Wieland, J.; Breit, B. *Nature Chem.* **2010**, *2*, 832.
- Breit, B.; Seiche, W. *J. Am. Chem. Soc.* **2003**, *125*, 6608.
- (a) Gellrich, U.; Huang, J.; Seiche, W.; Keller, M.; Meuwly, M.; Breit, B. *J. Am. Chem. Soc.* **2011**, *133*, 964.  
(b) Beierlein, C. H.; Breit, B.; Paz Schmidt, R. A.; Plattner, D. A. *Organometallics* **2010**, *29*, 2521. (c) Breit, B.; Seiche, W. *Pure Appl. Chem.* **2006**, *78*, 249.
- Seiche, W.; Schuschkowski, A.; Breit, B. *Adv. Synth. Catal.* **2005**, *347*, 1488.
- Straub, A. T.; Otto, M.; Usui, I.; Breit, B. *Adv. Synth. Catal.* **2013**, *355*, 2071.
- Fuchs, D.; Rousseau, G.; Diab, L.; Gellrich, U.; Breit, B. *Angew. Chem. Int. Ed.* **2012**, *51*, 2178.
- Agabekov, V.; Seiche, W.; Breit, B. *Chem. Sci.* **2013**, *4*, 2418.
- Kemme, S. T.; Smejkal, T.; Breit, B. *Chem.–Eur. J.* **2010**, *16*, 3423.