## Category

Organo- and Biocatalysis

## Key words

ionic [2+4] cycloaddition

cooperative catalysis

Diels-Alder reaction

thiophosphoramides

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Thiophosphoramide-Based Cooperative Catalysts for Brønsted Acid Promoted Ionic Diels-Alder Reactions *Angew. Chem. Int. Ed.* **2013**, *52*, 13424–13428.

## **Cooperative Catalysis in Ionic [4+2] Cycloadditions**



**Significance:** The Nagorny group reports an ionic [4+2] cycloaddition between  $\alpha$ , $\beta$ -unsaturated acetal dienophiles **1** and dienes **2** to afford Diels–Alder adducts **3** in moderate to excellent yields. The reaction is promoted by a cooperative catalytic system involving a strong Brønsted acid [PTSA (*p*-toluenesulfonic acid)] and a triple hydrogen bond donor thiophosphoramide (**A**). NMR and computational studies suggest that the key feature of the catalytic system is the strong interaction between **A** and the sulfonate anion.

**Comment:** Ionic [4+2] cycloadditions (Gassman's cycloadditions) have proven to be efficient complements to traditional Diels–Alder reactions when challenging unactivated substrates are involved. The authors report a variety of these reactions, which interestingly do neither require a Lewis acid nor a highly ionic medium for the generation of the reactive separated ion pair. The same objective is achieved by a cooperative catalytic system in which the sulfonic acid generates the oxocarbenium species and in which the thiophosphoramide co-catalyst ensures the formation of separated, highly reactive counterions via three hydrogen bonds to the sulfonate anion.

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