Cooperative Catalysis in Ionic [4+2] Cycloadditions

**Significance:** The Nagorny group reports an ionic [4+2] cycloaddition between α,β-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 thiophosphoramidic co-catalyst ensures the formation of separated, highly reactive counterions via three hydrogen bonds to the sulfonate anion.

**Selected examples:**

- **92% yield**
  - endo/exo = 4.4:1

- **85% yield**
  - endo/exo = 4.8:1

- **63% yield**
  - endo/exo = 4.8:1

**Proposed activation mode:**

The high yield and selectivity of the reaction are attributed to the strong interaction between the thiophosphoramide and the sulfonate anion, which generates a highly reactive, ‘naked’ oxocarbenium ion. The formation of separated counterions is facilitated by three strong hydrogen bonds.