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 not 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.