Metal-Organic Frameworks, the Switch to the Improbable: Lewis Acidic Phosphonium Ions Catalyse Aldol-Tishchenko Reaction

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The development of efficient catalytic methods is crucial for nowadays endeavors to achieve a good economic and ecologic efficiency in organic syntheses. In this respect, phosphines play a pivotal role to ensure high reactivity and selectivity. Their main application lies in the field of transition metal catalyzed reactions,[1] but phosphorous compounds gain increased interest in organocatalytic reactions; especially C-C bond forming ones from activated alkenes, allenes, and alkynes.[2]

The strong nucleophilic nature of phosphines facilitates the reaction with unsaturated carbon atoms forming zwitterionic phosphonium species that makes such carbon atoms more reactive towards nucleophilic attacks, enabling a variety of different C-C bond forming reactions, such as Michael addition and Morita-Baylis-Hillman (MBH) reaction.[2] Even though phosphonium cations have shown to catalyze different coupling reactions, such as Mukaiyama-aldol[3] and other C-C, C-N and C-O bond formations,[4] they are rarely reactive moieties – if ever – when in a zwitterion.

In this contribution, we describe a triphenylphosphonium zwitterionic species that unprecedentedly catalyzes the Aldol- Tishchenko (AT) reaction *only* when metal-organic frameworks (MOFs) are introduced in the reaction mixture. The reactivity of a zwitterionic phosphonium intermediate produced by the reaction of triphenylphosphine (PPh3) with methyl vinyl ketone (MVK) was changed with a MOFs additive with MOF-5 and UMCM-1 topologies. Such intermediate is the key to generating MBH products in the presence of aliphatic aldehydes and normally acts as a precursor to form C-C bonds, but it reacts as Lewis acid through the phosphonium moieties when MOFs are added leading to the AT reaction of the aldehyde. These findings show that the presence of MOFs can completely alter the reactivity of a zwitterionic phosphonium organocatalyst from a nucleophile in solution to an electrophile in the framework. This switch in reactivity enables improbable, yet undescribed reaction pathways, which would not happen under standard reaction conditions.

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