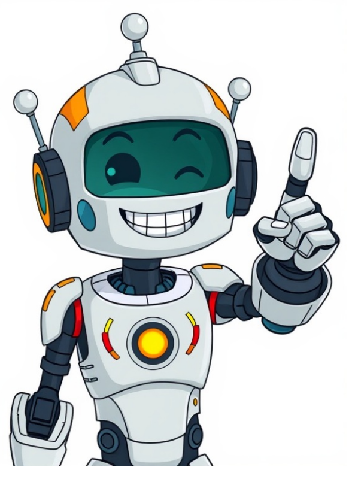
Click to prove you're human



thiolene based michael addition reactions utilized various catalysts, including primary and tertiary amines, as well as phosphines, to react thiols with dimers and oligomers of (meth)acrylates. These primary and tertiary amines were found to be efficient catalysts but required several hours to reach high conversion rates. the final say on how things turn out has been reserved for the most powerful of rulers. =================================== The molecular interactions between X2 catalysts and methyl acrylate are analyzed using state-of-the-art computational methods to understand their catalytic activity. The parent aza-Michael reaction is used as a model system, involving pyrrolidine and methyl acrylate, which has been experimentally studied by Borah et al. The interaction energy plays a critical role in determining the reactivity trends observed in the Michael addition reactions. A deeper analysis reveals that the acceleration of X2-catalyzed reactions originates from a more stabilizing interaction energy along the entire reaction coordinate and also from a less destabilizing strain, albeit to a lesser extent. =================================== The dihalogen catalysis of the Michael addition reactions is attributed to a novel electronic mechanism that differs from the traditional Lewis acidity enhancement hypothesis. =================================== Schematic orbital interaction diagram between the π-HOMO of methyl acrylate and the σ*-LUMO of X2 for 2 a (X2=F2) and 5 a (X2=I2), resulting in reduced π orbital amplitude on the terminal carbon atom involved in the forming C−N bond. =================================== The computed frontier molecular orbital (FMO) gaps and overlaps show that the FMO energy gaps for the HOMOpy–LUMO1 a–5 a interaction decrease, ranging from 6.1 to 5.4 eV for the uncatalyzed and I2-catalyzed reactions, respectively. =================================== The computed orbital overlap decreases significantly from S=0.19 to 0.13 for reactions 1 and 5, respectively, due to poorer orbital overlap caused by the polarization of the LUMO away from the C=C double bond by the dihalogen.In organometallic chemistry, pnicogen bonding is a type of metal-metal interaction involving phosphorus and/or arsenic atoms. This type of bond is crucial in understanding the reactivity of transition metal complexes and their relation to the properties of main group elements. =================================== The concept of pnicogen bonding was first proposed by Hammond G. S., who introduced it as a means of explaining the unusual reactivity of phosphorus-containing organometallic compounds. The idea gained momentum through various theoretical studies, including those by Bickelhaupt F. M. and Houk K. N. =================================== Recent advances in computational chemistry have allowed researchers to investigate the nature of pnicogen bonding using advanced theoretical methods. For instance, Zhao L., von Hopffgarten M., Andrada D. M., and Frenking G. employed a combination of density functional theory and molecular mechanics to explore the reaction mechanisms of phosphorus-containing compounds. =================================== One of the key aspects of pnicogen bonding is its relation to the Pauli repulsion term, ΔE Pauli, which arises from the antisymmetrization of the Hartree wavefunction. This term can significantly impact the reactivity trends in metal-metal interactions. ===================================The ability to form decisive bonds in organic chemistry transformations is crucial, such as in Diels-Alder cycloadditions, acetylene trimerization, and SN2 reactions. For example, García-Rodeja Y., Solà M., Fernández I. have published a paper on Phys. Chem. Chem. Phys. 2018, 20, 28011, where they demonstrated the importance of catalysts in enhancing the efficiency of these reactions. Another study by Yu S., de Bruijn H. M., Svatunek D., Hamlin T. A., Bickelhaupt F. M. on ChemistryOpen 2018, 7, 995 shows that enzymatic catalysts can play a significant role in stereoselective Michael Addition. The use of catalysts is also discussed in the paper by van Bochove M. A., Swart M., Bickelhaupt F. M. on J. Am. Chem. Soc. 2006, 128, 10738. Catalysts can be classified into different types, including enzymatic, organocatalytic, and metal-catalytic systems. Enzymatic catalysts, such as aldolases, are highly specific and operate under environmentally benign conditions. Organocatalysts, such as proline and thioureas, offer operational simplicity, low toxicity, and the ability to catalyze reactions in aqueous media. In contrast, metal-catalytic systems, such as palladium, copper, and nickel, can coordinate with reactants to form intermediates that facilitate nucleophilic addition. These catalysts are particularly effective in asymmetric Michael Additions, enabling the formation of enantiomerically pure products. The mechanism of catalyzed Michael Addition involves the activation of the α,β-unsaturated carbonyl compound by the catalyst. For instance, metal complexes can coordinate with the carbonyl group, increasing its electrophilicity. Simultaneously, nucleophiles are activated to form reactive carbanions, which then add to the β-carbon of the α,β-unsaturated carbonyl compound. The Michael Addition is extensively used in the synthesis of various organic compounds, including pharmaceuticals and natural products. Its ability to form carbon-carbon bonds in a stereocontrolled manner makes it invaluable in complex molecule construction.The liberating principles of the Creative Commons license empower creators to freely adapt, remix, and transform their work for any purpose, commercially or otherwise. =================================== The Michael addition is a type of organic reaction that involves the conjugate addition of a carbonyl compound (such as an aldehyde or ketone) to an α,β-unsaturated compound (such as an enone). This reaction is thermodynamically controlled and is typically performed in polar protic solvents.The Michael reaction is a crucial tool in organic chemistry for the selective formation of carbon-carbon bonds. It involves the nucleophilic attack of an enolate or other nucleophile on an α,β-unsaturated carbonyl compound, resulting in the creation of a new carbon-carbon bond at the β-carbon position. The Michael reaction involves electron-withdrawing groups such as acyl, cyano, nitro, or sulfone substituents that make adjacent methylene hydrogen acidic enough to form a carbanion when reacted with a base. This reaction typically occurs between an alkene (the Michael acceptor) and a nucleophile, which can be enolates of ketones or aldehydes, or other carbon-centered nucleophiles. The proline base is modified to work with a protic acid like p-toluenesulfonic acid, resulting in high selectivity and 99% ee. This occurs due to the enamine formed between the proline nitrogen and the cycloketone being co-facial with the nitro group hydrogen bonded to the protonated amine in the proline side group. The Michael Addition reaction is a widely used organic reaction in the synthesis of complex molecules. It involves the addition of an enolate to an α,β-unsaturated ketone or aldehyde, resulting in the formation of a new carbon-carbon bond. =================================== New organocatalysts derived from phenylglycine have been developed to produce optically active warfarin, a widely used anticoagulant. This breakthrough has significant implications for the synthesis of complex molecules and demonstrates the potential of organocatalysis in modern chemistry. According to recent studies, researchers have successfully employed titanium tetrachloride as an effective catalyst in various organic reactions, including the synthesis of bullvalones. These findings highlight the versatility and efficiency of this reagent in achieving complex transformations. The 1,4-addition reaction, a crucial step in many synthetic pathways, has been optimized through the development of novel organocatalysts. By fine-tuning the catalyst's structure and properties, chemists have achieved unprecedented levels of enantioselectivity, paving the way for more efficient and environmentally friendly synthesis. Moreover, advancements in covalent drug discovery have led to the development of new therapeutic agents with improved efficacy and reduced side effects. This has opened up new avenues for researchers to explore the potential applications of these compounds in various fields of medicine. In addition to these breakthroughs, recent studies on polymerization kinetics have shed light on the structural effects of thiol and vinyl monomers on the reaction mechanism. These findings provide valuable insights into the design and optimization of new polymeric materials with tailored properties. The discovery of indium-catalyzed block copolymerization has further expanded the scope of polymer synthesis, enabling the production of complex materials with unique characteristics. This innovation holds significant promise for a wide range of applications, from biomedical devices to advanced composites. Finally, researchers have been exploring the potential of conducting polymers in various technological applications, including energy storage and conversion. Their investigations into the redox properties of poly(2-methyl-5-amino-1,4-naphthoquinone) have provided valuable insights into the behavior of these materials under different conditions. ===================================Looking forward to seein everyone at the meeting tomorow and discussin our strategies. ===================================