

Editorial Note on Enolate Anions

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EDITORIAL

Enolates, also known as oxyallyl anions, are flexible reagents that may be used to make α -substituted carbonyl compounds, making them crucial intermediates in the synthesis of complex molecules. Because the stereochemical result of an enolate reaction is typically determined by the geometry of the enolate, enolate production is a crucial stage in many bond-forming reactions.

The counterion of an enolate has a significant impact on competing enolate reaction transition states. Cation chelation by the carbonyl oxygen atom and one or more additional basic parts of the reactants is frequently the cause of the effect. Alkylation of chiral enolates, for example, can produce more or less diastereomerically pure products, and selectivity is frequently determined by the counterion.

Because the counterion is so important in controlling enolate reaction product distributions, the synthetic chemist must have stereoselective procedures for preparing enolate anions with a variety of counterions on hand. There are multiple sections in this chapter. The ten sections that follow cover current methods for preparing Li, Mg, B, Al, Sn, Ti, Zr, Cu, Zn, and other transition metal enolates.

There are only two types of enolates: those with the metal closer to the oxygen atom and those with the metal closer to the carbon atom. Enolates from Groups I, II, and III exist as O-metal tautomers. These highly electropositive metals form a strong bond with the oxygen atom. Both forms of enolates are found in transition metal enolates. The cation is related with a delocalized state in a few transition metal enolate anion (η^3 -enolate complexes).

Magnetic resonance studies (NMR) and X-ray crystallography have been used to investigate the structures of enolates. 2–12 Depending on the enolate structure, the type of the cation, and the solvent, solvated enolates occur as dimers, tetramers, or hexamers enolate does not affect the (E)/(Z) nomenclature.

Throughout this chapter, the following nomenclature for enolate stereoisomers will be used: With one exception, the (E)/(Z) nomenclature follows the Cahn-Ingold-Prelog criteria. The OM (oxy-metal) group is defined as having the highest priority at the

carbonyl C-atom, regardless of the type of the metal, this has the advantage of allowing you to change the metal you're working with.

Enolate Ions Alkylation

Nucleophiles are enolates, which are created when a strong base abstracts the hydrogen atom. As bases, lithium diisopropylamide (LDA) or sodium hydride are needed. The acidity of the two potential hydrogen atoms is connected to the location of proton abstraction, which is in the order primary > secondary > tertiary.

Alkylated ketones are formed when an enolate reacts with an alkyl halide. Proton exchange between the original enolate and the alkylated ketone, followed by alkylation of that enolate ion, might result in multiple alkylation.

Silyl Enol Ethers and Enolates from Enol Esters

Enolates can also be made by reacting alkyl lithium reagents with enol esters silyl enol ethers. House devised a method for allowing these enolates to react with aldehydes to produce the appropriate aldols.

When lithium enolate is produced in ether or 1,2-dimethoxyethane (DME) by reacting an enol acetate with methyl lithium, higher quantities of aldol compounds are obtained. If the enolate is made by reacting a silyl enol ether with methyl lithium, the yields are lower. THF is inferior to ether or mixes of ether and DME in the aldol process.

At low temperatures (-20 to 50°C), acceptable yields of aldol adducts can be produced in ether. The addition of anhydrous ZnCl_2 or MgBr_2 to the more polar solvents DME or THF leads in better yields. In equation, you may see an example.

Reorganization of Enolates

2,3-Wittig rearrangements produce α -hydroxy carbonyl compounds from enolates generated from α -allyloxy acids, esters, and amides. For example, excessive LDA treatment of ester 192 produces dianion 193, which is stereoselectively transformed to 195 by 2,3-Wittig rearrangement and aqueous workup. This reaction takes place at transition state 194, where the enolate has an endo-relationship with the alkene-system (which is commonly observed in enolate 2,3-Wittig rearrangements).

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