

Recent developments in the chemistry of cyclic morita- baylis- hillman adducts

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Abstract

An allyl is a substituent with the molecular formula $H_2C=CH-CH_2R$. It consists of a radical bridge ($-CH_2-$) hooked up to a vinyl radical ($-CH=CH_2$). The name springs from the Latin word for garlic, *Allium sativum*. In 1844, Theodor Wertheim isolated an allyl group by-product from garlic oil and named it "Schwefelallyl. The term allyl group applies to several compounds associated with $H_2C=CH-CH_2$, a number of that square measure of sensible or of everyday importance, as an example, allyl group chloride. The allyl is wide encountered in chemical science. Radicals, anions, and cations square measure usually mentioned as intermediates in reactions. All feature 3 contiguous sp^2 -hybridized carbon centres and every one derive stability from resonance. Every species will be bestowed by 2 resonance structures with the charge or mismatched lepton distributed at each one,3 positions. Allylation is any chemical action that adds an allyl to a substrate

Carbonyl allylation: Typically allyl group refers to the addition of an allyl ion cherish an organic electrophile Carbonyl allylation could be a variety of organic reaction during which an activated allyl is superimposed to chemical group manufacturing an radical tertiary alcohol.

Conjugate addition

Organ tantalum reagents square measure helpful for conjugate addition to enones. Of specific interest is that the ability of sure organ tantalum reagents to market the conjugate allylation of enones.

Many substituents will be hooked up to the allyl to grant stable compounds. Commercially necessary allyl group compounds include: alcohol ($H_2C=CH-CH_2OH$), allyl group chloride($H_2C=CH-CH_2Cl$), Crotyl alcohol ($CH_3CH=CH-CH_2OH$), Dimethylallyl salt, central within the biogenesis of terpenes, a precursor to several natural merchandise, as well as natural rubber. Transition-metal allyl group complexes, like allylpalladium chloride compound

The Baylis–Hillman reaction is a reaction between the α -position of AN activated olefine and a carbon electrophile like an compound. employing a nucleophilic catalyst, sort of a tertiary methane series and gas, this reaction provides a densely functionalized product (e.g. functionalized alcohol within the case of compound because the electrophile). It's named for Anthony B. Baylis and Melville E. D. Hillman, World Health Organization developed this reaction whereas working at Celanese. This reaction is additionally mentioned because the Morita–Baylis–Hillman reaction or MBH reaction.

DABCO is one amongst the foremost often times used tertiary alkane series catalysts for this reaction. Additionally, nucleophilic amines like DMAP and DBU yet as phosphines are found to with success change state this reaction.

MBH reaction has many blessings as a helpful artificial method: 1) it's

AN atom-economic coupling of simply ready beginning materials. 2) Reaction of a pro-chiral electrophile generates a chiral center, so an uneven synthesis is feasible. 3) Reaction merchandise sometimes contain multiple functionalities in an exceedingly proximity in order that a spread of more transformations square measure attainable. 4) It will use a nucleophilic organo-catalytic system while not the utilization of serious metal beneath delicate conditions.

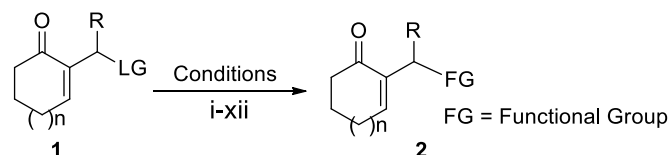
Limitations as a result of there's a good extent of variability in reaction substrates, it's usually difficult to develop reaction conditions appropriate surely combination of substrates. As an example, β -substituted activated olefins, vinyl sulfones, and vinyl sulfoxides exhibit low reactivities, retardation or preventing reaction. Competitory reactions of substrate functionalities are problematic. Acroleins square measure vulnerable to oligomerization, and allenates simply endure cycloaddition reactions. It's extraordinarily exhausting to develop appropriate conditions for victimization alkyl group halides and epoxides as electrophiles.

Despite broad scope, atom economy, and generality of the reaction, the slow rate of the Baylis-Hillman reaction (reaction times of a period or maybe longer don't seem to be uncommon, even with twenty five to a hundred metric weight unit nothing catalyst) for hindered open-chain aldehydes and electron-rich benzaldehydes usually limits the artificial utility of the method. As an example, within the case of sterically hindered t-butyl propenoate, reaction with benzaldehyde with DABCO as catalyst within the absence of solvent needs four weeks to grant moderate levels of conversion to the specified product. Within the presence of aprotic solvents, the reaction rate is even slower, though protic additives (e.g., alcohols and radical acids) could accelerate the reaction. Ketones square measure typically not reactive enough to require half within the reaction in an exceedingly synthetically helpful manner beneath normal conditions. However, because of the extremely negative volume of activation, sluggish Baylis-Hillman reactions, as well as those victimization ketones as substrates, will be realised by conducting the reaction beneath high (up to 20 kbar)

High reactivity of the activated olefine might even be a tangle. The MBH reaction of an aryl vinyl organic compound with an organic compound isn't easy, since the reactive aryl vinyl organic compound pronto adds 1st to a different molecule of aryl vinyl organic compound via Michael addition, then the adduct adds to the organic compound to create a double MBH adduct

Functionalized allylic compounds are useful tools in organic chemistry and for the synthesis of biologically active targets. During the last decades, the Morita-Baylis-Hillman (MBH) adducts have attracted much attention. A large number of synthetic applications, respecting the atom economy and implementing the organocatalysis in aqueous medium or under solvent-free conditions, have been reported by our research group.

We focus herein on the synthesis and transformations of differently functionalized allylic compounds **2** derived from the MBH alcohols **1** (Scheme 1).



$n = 0, 1$; LG = OH, OAc; R = H, alkyl, aryl

Scheme 1: Conversions of MBH adducts **1** into various allylic compounds **2**.

Reagents and conditions: (i) R=H, □-dicarbonyl compounds, DMAP; (ii) R=H, □ □-dicarbonyl compounds, Pd(OAc)₂, Et₃B; (iii) R=Ac, □□-dicarbonyl compounds, Et₃N; (iv) R=H, □-keto, esters, Et₃N; (v) R=Ac, amines; (vi) R=H, amines, molecular sieves; (vii) R=H,

amines, Pd(OAc)₂, Et₃B; (viii) R=Ac, RSH; (ix) R=H, RSH, *p*-TsOH; (x) R=H, RSH, molecular sieves; (xi) R=H, P(OEt)₃, DMAP, solvent-free; (xii) R=Ac, P(OEt)₃, DMAP, solvent-free; (xiii) R=Ac, cyclohexanone or cyclopentanone enamines, Pd(OAc)₂, ZnBr₂

Recent Publications

1. Rezgui F (2016) *Journal of Organic Chemistry*, 81:1757-1761.
2. Rezgui F (2016) *Bio Organic Chemistry*, 78, 24-28.
3. Rezgui F (2018) *Journal of Molecular Structure*, 1127:169-174.
4. Rezgui F (2017) *Tetrahedron Lett.* 58, 2525-2529.
5. Rezgui F (2016) *Synthetic communications* 46:1796-1802.
6. Rezgui F (2014) *Synlett* 25:2196-2200.