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Spotlight 366

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Enol Acetates

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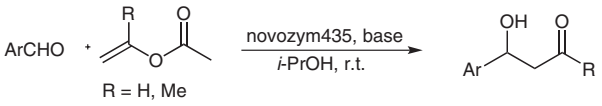
Introduction

Enol acetates have enjoyed unique importance as intermediates in organic synthesis with a wide range of applications.[1] The enol acetates are mainly employed in the transesterification of alcohols to synthesise chiral alcohols and acetates in high enantiomeric excess catalyzed by biocatalysts, such as lipases,[2] as well as the catalysts, such as iodine,[3] $Cp_2Sm(thf)_2$,[4] diethylzinc,[5] etc. They also find applications in the synthesis of biologically active intermediates like 1-acetyladamantane,[6] used as the starting material in the efficient preparation of the anti-influenza drug rimanadine and natural products, such as saponaceolides,[7] briarellin J,[8] etc.

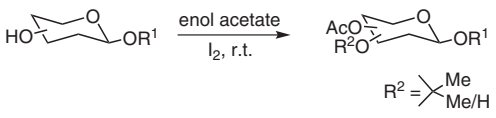
Enol acetates are commercially accessible. Acetates of cyclic ketones can be easily prepared using perchloric acid and acetic anhydride.[9] Isopropenyl acetate is prepared on commercial scale by a sulfuric acid catalyzed reaction of acetone and ketene.[10] Whereas, the vinyl ester can be obtained by the reaction of ethylene and acetic acid with oxygen in the presence of palladium catalyst.[11] Besides, chiral enol acetates have also been synthesized from racemic enol acetates or ketones through multistep reactions catalyzed by lipase and a ruthenium complex.[12]

Abstracts

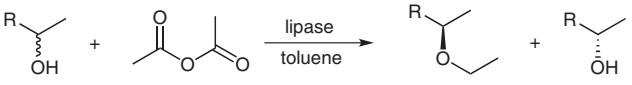
(A) Recently, Taneja and co-workers have employed enol acetates, for example vinyl and isopropenyl acetates, in aldol reaction catalyzed by a lipase in tandem with an organic base to afford cross-aldol products.[13]



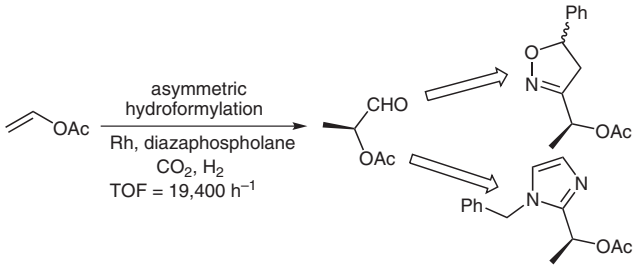
(B) In an earlier work by Mukherjee et al. enol acetates were utilized in the synthesis of various types of orthogonally protected sugar derivatives of simple sugars and their glycosides using molecular iodine as catalyst under solvent-free conditions.[14] The outcome of the reaction was controlled by variation of the temperature; at lower temperature acetonide acetate was obtained as a single product, whereas at higher temperature peracetate was the major product.



(C) Lipase-catalyzed kinetic resolution of racemates in the presence of an enol acetate is a versatile method for the separation of enantiomers. The method can be used in the resolution of primary, secondary and tertiary alcohols as well as chiral carboxylic acids and diols.[15]



(D) The vinyl acetate has been hydroformylated asymmetrically to afford (*R*)- and (*S*)-2-(acetyloxy)propanal, which can be utilized in the asymmetric synthesis of chiral isoxazolines and imidazoles.[16]



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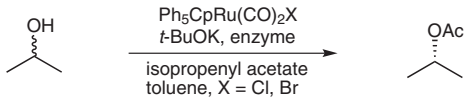
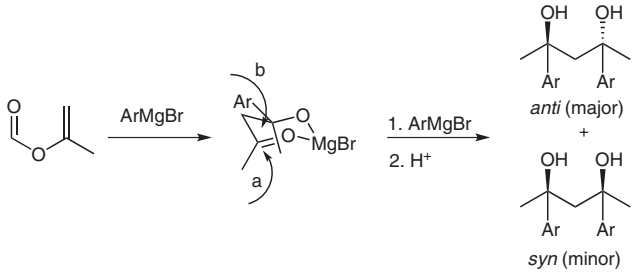
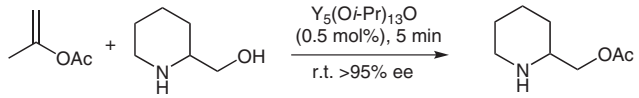
(E) Bäckvall and co-workers successfully exploited $Ph_5CpRu(CO)_2X$ complexes as catalysts for the racemization of secondary alcohols at ambient temperature, which in tandem with enzymatic resolution of the alcohols resulted in a highly efficient synthesis of enantiomerically pure acetates via dynamic kinetic resolution (DKR).[17] The reaction is applicable to a wide range of functionalized alcohols including heteroaromatic alcohols.



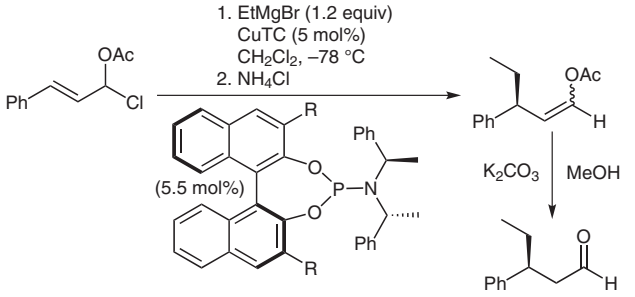
(F) Jiao et al. synthesized a series of symmetrical aromatic 1,3-diols using isopropenyl acetate and substituted aryl Grignard reagents in a one-step reaction.[18] The 1,3-diol moiety is present in a number of natural products, including polyene macrolide antibiotics.



(G) Both vinyl or isopropenyl acetate have also been used in the transesterification of primary and secondary alcohols in the presence of catalytic amounts of $Y_5(Oi\text{-}Pr)_{13}O$. The Yttrium catalyst promotes the selective O-acylation of amino alcohols without amide formation.[19]



(H) Feringa and Mastral reported the transformation of α,β-unsaturated aldehydes into α-chloroallylic acetates, which on subsequent copper-catalyzed regio- and enantioselective allylic alkylation with Grignard reagents provided chiral enol acetates and eventually chiral substituted aldehydes in a one-pot protocol (up to 94% ee).[20]



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