

SYNLETT Spotlight 331

3-Methyl-2-Butenal

Compiled by Claiton Pires Ventura

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

Introduction

3-Methyl-2-butenal, also known as 3,3-dimethylacrolein, is a very interesting reagent used in addition and cycloaddition reactions. This colorless, light-yellowish liquid has a pungent odor and is miscible in common organic solvents and water. It is commercially available, but it can also be prepared by oxidation of 3-methyl-2-butenol with H₂O₂. Kon et al. have reported this reaction with a yield of 91%.¹

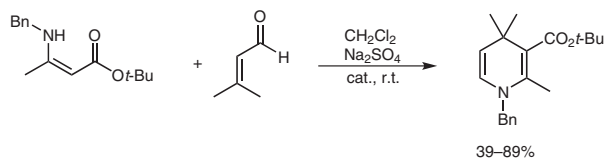
3-Methyl-2-butenal is an α,β -unsaturated carbonyl compound. This compound has interesting properties that re-

sult from the conjugation of the carbon-carbon double bond with the carbonyl group and the two electrophilic sites: The carbonyl carbon and the carbon atom that is in β -position to it. The polarization of electron density makes their β -carbon atoms rather electrophilic.²

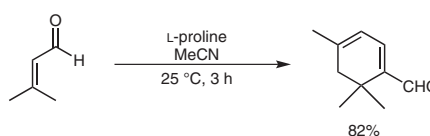
Various examples of the use of 3-methyl-2-butenal are found in the literature. This reagent has been explored for the preparation of 1,4-dihydropyridines,³ diene adducts,⁴ pyranonaphthoquinones,⁵ nitropentanal pyrrole,⁶ cyclization precursors,⁷ and 2*H*-chromenes.⁹

Abstracts

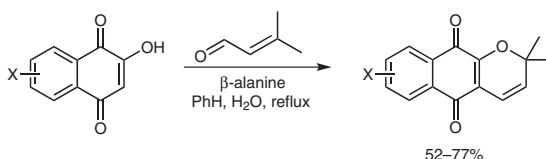
(A) Moreau et al. reported on the addition of β -enaminoacrylates to α,β -unsaturated aldehydes catalyzed by a metal-free Brønsted acid, which provides 1,4-dihydropyridines. The substituted dihydropyridines were obtained in moderate to good yields under mild conditions.³



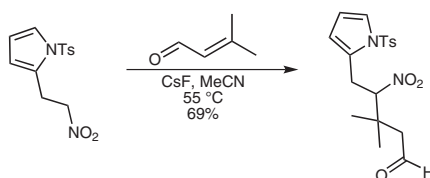
(B) Hong et al. studied a series of homologous unsaturated aldehydes which were then reacted with L-proline in acetonitrile to afford the corresponding adducts. The reaction of 3-methyl-2-butenal with L-proline afforded a diene adduct in 82% yield via formal [4+2] cycloaddition.⁴



(C) The reaction of some naphthoquinones, α,β -unsaturated aldehyde, and β -alanine affords pyranonaphthoquinones via one-pot 6π -electrocyclization in modest to good yields (52–77%). These substances are potential carcinogenesis inhibitors.⁵



(D) The Michael addition of *N*-*p*-tosyl nitroethylpyrrole with 3-methyl-2-butenal in the presence of CsF gave the nitropentanal pyrrole, an important intermediate in the synthesis of hydrodipyrins, in 69% yield.⁶



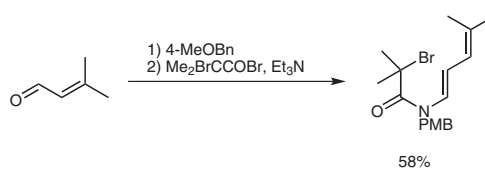
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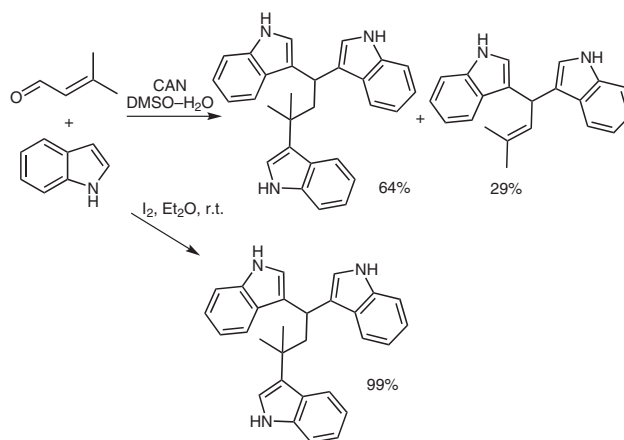
DOI: 10.1055/s-0030-1258564; Art ID: V33810ST

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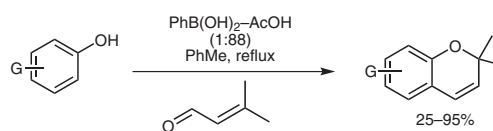
(E) The condensation of 3-methyl-2-butenal with *p*-methoxybenzylamine followed by triethylamine-mediated acylation with 2-bromo-2-methylpropionyl bromide produced an important cyclization precursor.⁷



(G) Ko et al. reported on cerium ammonium nitrate (CAN) and iodine-catalyzed reactions of indole or 1-methylindole with α,β -unsaturated ketone or aldehyde. The reaction of 3-methyl-2-butenal with indole shows different results when CAN and iodine were used as catalysts.⁸



(H) Chauder et al. reported an important condensation of phenols with 3-methyl-2-butenal in the presence of phenylboronic acid in an acetic acid/toluene solution that leads to substituted and condensed 2*H*-chromenes. This work constitutes a mild and advantageous complement to classical routes for these heterocycles.⁹



References

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