

# SYNLETT Spotlight 331

## 3-Methyl-2-Butenal

Compiled by Claiton Pires Ventura

Claiton Pires Ventura was born in Minas Gerais, Brazil in 1978. He received his B.Sc. degree in pharmacy from the Universidade Federal de Minas Gerais in 2001 and his M.Sc. in pharmacy from the same university in 2003. He is currently working toward his Ph.D. under the supervision of Professor Rosemeire Brondi Alves. His research interests focus on the synthesis of pterocarpanes from 2*H*-chromenes.

Instituto de Química, Universidade Federal de Minas Gerais, UFMG,  
CEP 31270-901 Minas Gerais, Brazil  
E-mail: xclaiton@gmail.com



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 H<sub>2</sub>O<sub>2</sub>. Kon et al. have reported this reaction with a yield of 91%.<sup>1</sup>

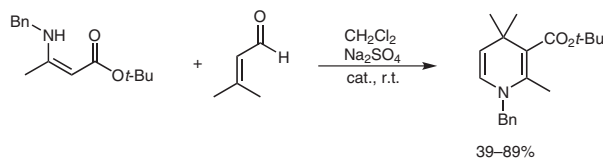
3-Methyl-2-butenal is an  $\alpha,\beta$ -unsaturated carbonyl compound. This compound has interesting properties that re-

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  $\beta$ -position to it. The polarization of electron density makes their  $\beta$ -carbon atoms rather electrophilic.<sup>2</sup>

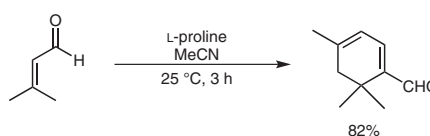
Various examples of the use of 3-methyl-2-butenal are found in the literature. This reagent has been explored for the preparation of 1,4-dihydropyridines,<sup>3</sup> diene adducts,<sup>4</sup> pyranonaphthoquinones,<sup>5</sup> nitropentanal pyrrole,<sup>6</sup> cyclization precursors,<sup>7</sup> and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

### Abstracts

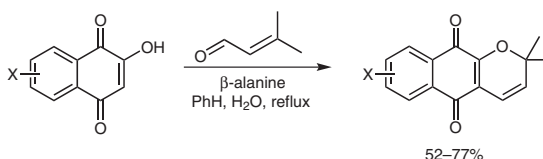
(A) Moreau et al. reported on the addition of  $\beta$ -enaminoacrylates to  $\alpha,\beta$ -unsaturated aldehydes catalyzed by a metal-free Brønsted acid, which provides 1,4-dihydropyridines. The substituted dihydropyridines were obtained in moderate to good yields under mild conditions.<sup>3</sup>



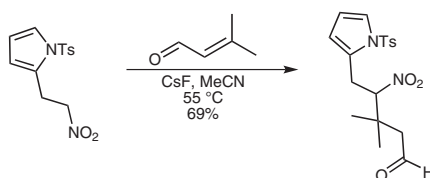
(B) Hong et al. studied a series of homologous unsaturated aldehydes which were then reacted with L-proline in acetonitrile to afford the corresponding adducts. The reaction of 3-methyl-2-butenal with L-proline afforded a diene adduct in 82% yield via formal [4+2] cycloaddition.<sup>4</sup>



(C) The reaction of some naphthoquinones,  $\alpha,\beta$ -unsaturated aldehyde, and  $\beta$ -alanine affords pyranonaphthoquinones via one-pot  $6\pi$ -electrocyclization in modest to good yields (52–77%). These substances are potential carcinogenesis inhibitors.<sup>5</sup>



(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.<sup>6</sup>



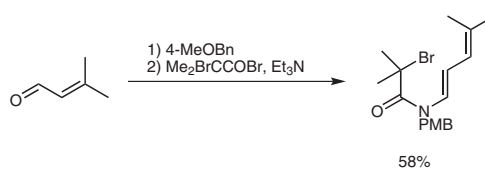
SYNLETT 2010, No. 17, pp 2677–2678

Advanced online publication: 30.09.2010

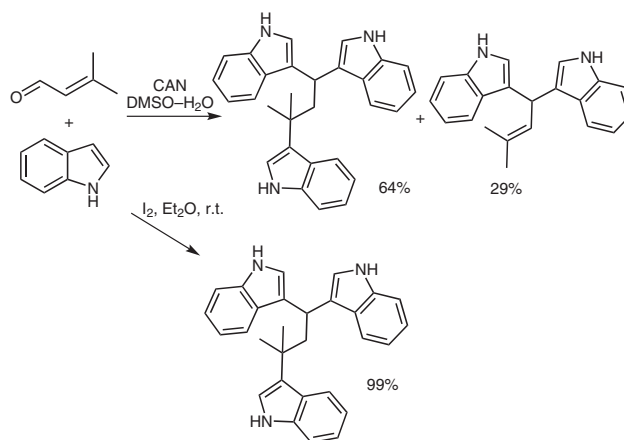
DOI: 10.1055/s-0030-1258564; Art ID: V33810ST

© Georg Thieme Verlag Stuttgart · New York

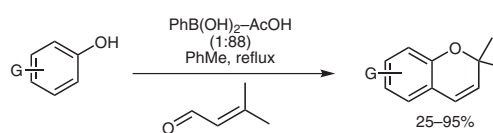
(E) The condensation of 3-methyl-2-butenal with *p*-methoxybenzylamine followed by triethylamine-mediated acylation with 2-bromo-2-methylpropionyl bromide produced an important cyclization precursor.<sup>7</sup>



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



(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.<sup>9</sup>



## References

- (1) Kon, Y.; Usui, Y.; Sato, K. *Chem. Commun.* **2007**, 4399.
- (2) Carey, F. A. *Organic Chemistry*; McGraw-Hill: New York, .
- (3) Moreau, J.; Duboc, A.; Hubert, C.; Hurvois, J.; Renaud, J. *Tetrahedron Lett.* **2007**, *48*, 8647.
- (4) Hong, B.; Wu, M.; Tseng, H.; Liao, J. *Org. Lett.* **2006**, *8*, 2217.
- (5) Kumar, S.; Malachowski, W. P.; DuHadaway, J. B.; La Londe, J. M.; Carroll, P. J.; Jaller, D.; Metz, R.; Prendergast, G. C.; Muller, A. J. *J. Med. Chem.* **2008**, *51*, 1706.
- (6) Kim, H.; Dogutan, D. K.; Ptaszek, M.; Lindsey, J. S. *Tetrahedron* **2007**, *63*, 37.
- (7) Clark, A. J.; Geden, J. V.; Thom, S.; Wilson, P. *J. Org. Chem.* **2007**, *72*, 5923.
- (8) Ko, S.; Lin, C.; Tu, Z.; Wang, Y.; Wang, C.; Yao, C. *Tetrahedron Lett.* **2006**, *47*, 487.
- (9) Chauder, B. A.; Lopes, C. C.; Lopes, R. S. C.; da Silva, A. J. M.; Snieckus, V. *Synthesis* **1998**, 279.