Regioselective and reductive cleavage of allyl ethers by NaBH₄-HOAc

Yen-Bo Chen ^a, Zi-Ping Lin ^a, Chen-Yin Chen ^a, Po-Yen Chen ^a, Chun-Hung Lin ^b, Min-Tsang Hsieh ^c, Jin-Cherng Lien ^a, Yin-Hsuan Chou ^a, Hui-Chang Lin ^{a,*}

β-Enaminals were successfully synthesized in good to excellent yields by the reaction of C2-formylglycals with primary amines. Subsequent reaction with NaBH₄ in HOAc led to unexpected reductive cleavage of allyl ether, i.e., the hydrodealkoxylation took place to produce the corresponding 3-deoxy-β-enaminals. In contrast, the reaction of β-enaminals with Zn/HOAc performed H4-elimination to afford a diene product. The result was attributed to the formation of a common eneiminium ion intermediate, and the different reduction reactivity.

^a Graduate Institute of Pharmaceutical Chemistry, China Medical University, No. 91, Hsueh-Shih Rd., Taichung 40402, Taiwan

^b Institute of Biological Chemistry, Academia Sinica, No. 128, Academia Road, Section 2, Nan-Kang, Taipei 11529, Taiwan

^c Chinese Medicinal Research and Development Center, China Medical University Hospital, No. 2, Yude Rd., Taichung 40447, Taiwan