

Jagiellonian University

Faculty of Chemistry



Prof. Dr. Tad A. Holak
Tel: +48-12-663-2287
Email: holak@chemia.uj.edu.pl

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The Ph.D. thesis of Smita Basu entitled "Enantioselective Vinylogous Mukaiyama-Michael Reaction with Acyclic Silyl Dienolates" – submitted for the degree of Doctor of Philosophy at the Jagiellonian University – describes the vinylogous Mukaiyama-Michael reaction of vinylketene silylacetals and α,β -unsaturated aldehydes in the presence of an organocatalyst and a co-catalyst. The research work of Ms. Basu has been carried out under the supervision of Professor Christopher Schneider and Professor Jacek Młynarski, renowned organic chemistry scientists, whose current research focuses on the development and application of novel stereoselective synthetic methods for the control of relative and absolute configurations. The work presented by Ms. Basu falls within this area of research.

Ms. Basu is a co-author of 9 publications. Her thesis is comprised of 220 pages of text, tables, figures and schemes, organized into eight chapters. The first chapter briefly explains the importance of chirality in nature. This aspect is documented by numerous, well selected examples. The author also describes three major categories of catalysts used in asymmetric syntheses.

Chapter 2 of the thesis reports broad characterization of organocatalysis. The author presents historical background of organocatalysis, classification of a modern organocatalysis into two branches: the covalent and non-covalent catalysis. This part of the thesis includes a comprehensive discussion of the secondary amine catalysis *via* enamines or iminium ions, the H-bonding catalysis and the phase transfer catalysis-PTC. Here the author also briefly mentions the concept of the nucleophilic and Brønsted base catalysis, the SOMO-catalysis, and the di- and tri-enamine catalysis.

The vinylogous Mukaiyama-Michael reaction is presented in detail in chapter 3. The vinylogous Mukaiyama-Michael reaction is an important organic class of carbon-carbon bond forming reactions. The author of the dissertation also describes mechanistic pathways for the iminium-ion-catalyzed vinylogous Mukaiyama-Michael reaction. The most recent advances of this reaction are described at the end of this part of the thesis.

Chapter 4, entitled "Research Objectives", describes Ms. Basu's own research. Her research has concentrated on the synthesis of new dienolates for the vinylogous Mukaiyama-Michael reaction, using an iminium-ion catalysis mode. The products obtained in this reaction could be easily functionalized into other important synthons. Chapter 5 describes in detail the procedures and the results of the synthesis of the vinylketene silyl-*N,O*-acetals or silyl-*Si,O*-acetals, and α,β -unsaturated aldehydes in the vinylogous Michael reaction. The reactions were optimized by using different solvent systems, catalysts, co-catalysts, temperatures and time settings. Moreover, for compounds **159a** and **177a** efforts were made to determine the configuration of stereocenters by appropriate derivatization into known compounds (on the basis of the comparative NMR studies and the optical rotation). The author of the thesis also presented detailed interpretation of ^1H and ^{13}C NMR spectra of the Michael product **159a** described in this section.

Chapter 6 summarizes the most important results obtained during examination of the vinylogous Mukaiyama-Michael reaction, and chapter 7 presents the experimental details and methods. The compounds obtained by Ms. Basu have been characterized by analytical and spectroscopic methods. Finally, in chapter 8, the author cites 165 references (the majority of them published recently).

The presented Ph.D. thesis is well-written. The graphical layout of the thesis is of the highest standard. It has been a pleasure to read this dissertation. In view of the above, there is some carelessness with formatting. A few examples are provided below:

- The table caption should be typed above the table;
- p. 176; example 7.5.16.2. 5.93 (*ddd*, $J = 17.0, 10.2, 9.0$ Hz, 1H, *major*), 1H, *major*); - doubled words 1H and *major*;
- an erroneous date of year p. 43 is: "*The greatest milestone in organocatalysis came in the year 1950...*" should be: in the year 1960 (Pracejus' work has been published in 1960 – ref. 9);

- p. 101 "Gupta further showed that NMR and NOE experiments were consistent with the crystal structure..." – NOE experiments is one of the techniques of NMR spectroscopy – it is not a different type of spectroscopy, it should be more like: *Gupta further showed that ¹H, ¹³C and NOE NMR experiments were consistent with the crystal structure...*"

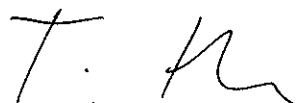
- The absence of the optical rotation in the experimental section for compounds **190**, **191** and **197**.

- Why the methanol is shown in the adduct ion of compounds **172b** and **174b**, if acetone was used in the ESI measurement?

- The significant figures of the data in the experimental details should have the same precision; for example: p. 143 7.3.1 Synthesis of compound **153**: *5.0 g of E-Crotonamide, 580 mg of p-Toluenesulphonic acid, 1.74 g of Na₂CO₃*;

The suggested corrections given above are not mandatory, but could be accommodated in a possible revised version in case one is made.

In conclusion, it is without reservation that I recommend that the Ph.D. thesis of Smita Basu entitled "Enantioselective Vinylogous Mukaiyama-Michael Reaction with Acyclic Silyl Dienolates" be accepted as meeting all dissertation requirements for the Doctor of Philosophy degree.



Tad Holak