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PREVIEW

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**I. Gas phase anion reactions: Transesterification, Claisen-Schmidt,
and water elimination from fatty acid carboxylates.
II. Fragmentation pathways of benzofuroxan and benzofurazan
derivatives**

Haas, George William, Ph.D.

The University of Nebraska - Lincoln, 1994

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PREVIEW

**I. GAS-PHASE ANION REACTIONS: TRANSESTERIFICATION,
CLAISEN-SCHMIDT, AND WATER ELIMINATION
FROM FATTY ACID CARBOXYLATES**

**II. FRAGMENTATION PATHWAYS OF BENZOFUROXAN AND
BENZOFURAZAN DERIVATIVES**

by

George W. Haas

A DISSERTATION

**Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy**

Major: Chemistry

Under the Supervision of Professor Michael L. Gross

Lincoln, Nebraska

August, 1994

DISSERTATION TITLE


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Water Elimination From Fatty Acid Carboxylates

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George William Haas

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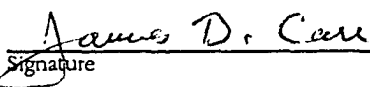

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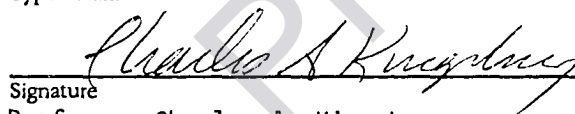
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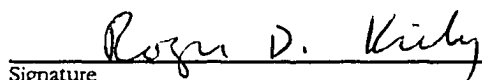
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George W. Haas, Ph.D.

University of Nebraska, 1994

Advisor: Professor Michael L. Gross

The major subject of this dissertation involves three gas-phase anion reactions: transesterification, Claisen-Schmidt, and water elimination from fatty-acid carboxylates. Tandem-sector and Fourier Transform mass spectrometers are employed for these investigations. Fatty acid carboxylates, desorbed into the gas phase by fast atom bombardment, undergo both metastable-ion and collisionally activated dissociation to eliminate water via an ion-neutral complex involving hydroxide ion and neutral ketene (Chapter 1). The gas-phase, base-catalyzed transesterification of acetate esters is described in Chapter 2. Evidence is presented from kinetics, equilibrium constants, and

thermochemically derived data that transesterification proceeds in the gas phase by the attack of the acetate enolate anion on alcohol. The formation of the larger alkyl acetate enolates is favored, which is in contrast to liquid-phase chemistry. The effect of substituents was investigated for the gas-phase, base-catalyzed Claisen-Schmidt reaction of the acetone enolate anion and various para-substituted benzaldehydes (Chapter 3). The Hammett constants for the substituents correlate the extent of stabilization of the negative charge in the formation of covalently bound adducts that eliminate water.

The second main part of this dissertation deals with the fragmentation pathways of benzofuroxan and benzofurazan derivatives. The loss of oxygen is investigated to discern whether it is a thermal degradation process or primarily an ionic process. In another study, the mechanism for the formation of fragment ions that can be used to distinguish between angular and linear isomers is elucidated.

Acknowledgments

There are a lot of friends, colleagues, professors, and family members that I would like to express a sincere thank you in appreciation for the intellectually inspiring and caring conversations throughout my graduate career at the University of Nebraska-Lincoln. I would first like to thank Professor Gross for allowing me to study mass spectrometry under his supervision. Dr. Gross, I will always remember discussing my research in the evening and into the night, as you have shown me ways of looking at my results and interpreting data that left me feeling we could conquer any problem.

Mr. Don Rempel, you simply amaze me with the knowledge you have accumulated. Don, I express sincere gratitude for your help with carrying out FTMS experiments on a real state of the art research instrument. I wish you happiness.

Dr. Daryl Giblin (kindly referred to as *Hobbes*), you are another special individual I need to thank. You keep the instruments operating and have rescued me from troubling problems more times than I can remember. I will always miss joking with you, "the graduate student's friend".

Dr. Ron Cerny, thank you for all the guidance and advice. You were the first person to educate me on how to operate a sector instrument and made the

complexities of operating them seem simple. You have been very supportive of me and of my education during my stay here, and oh yes, Have A Nice Day!!!!!!

A special group thanks go to the Professors on my graduate committee, which is comprised of Dr. James Carr, Dr. David Hage, Dr. Charles Kingsbury, and Dr. Roger Kirby. You professors have helped me think about research with a critical eye and become a better scientist.

My undergraduate professors who truly got me interested in chemistry, Dr. Smith, Dr. Schwartz, and Mrs. Heckel, thank you. You three are wonderful educators and I respect you three even more now, than when I graduated from Missouri Western State College.

Life in graduate school was a honor and a privilege to work beside past and present graduate students, Denise McMillian, Kenny Caldwell, Cliff Jacoby, Peifeng Hu, Jonathon Gooden, Todd Eary, Chris Holliman, Jaeman Byun, Paul Hopfer, Olga Nemirovskiy, Duane Reiber, David Vollmer, Joelle Wellemans, and Andy Whitehill. An extra thanks go to Steve Loecker and Scott McQueen for helping me with that other magnetic technique.

Kathy Schinstock and Lorraine Moon, thank you for helping me survive in the basement and listening to my seemingly endless problems. Kathy thanks again for all the little things you helped me with that seemed so monstrous at the time.

Les "Magic" Marquart and Mike "The Animal" Jensen, thanks for fixing things that I don't know how got broken!!!! Let's do lunch.

Mary Kay, thanks for all the library help and ordering literature for me at a last-minute deadline. You are a real blessing.

I am glad I have friends like John "Charge it" Richmond and Greg "the Life Saver" Krumme. A person does not have much if they do not have friends like you two. Thanks for the cards and calls, they were greatly appreciated.

Most of all, I take this time now to express how much I appreciated all the phone calls and letters from my family. Everybody should have supporting family members like mine. Thank you Tony for all that you have done. Norma June and Gary, you must have a sixth sense for knowing when to call me to cheer me up. Sister, thanks for lifting my spirits by coming up before the final deadline of my dissertation. Aunt Betzey, thanks for all the cards and stuff.

Mom and Dad, I have finally made it. Thanks for supporting me and believing in me when I did not. Words can not express how much I love you two, and I am proud to have parents like you two.

Well Sherie, I graduated. These times have tested our relationship, which has held true. I do not know how my graduate career would have turned out, without someone like you to share my triumphs and disappointments. You have been a reality check and I would like to grow old with you (read between the lines).

Success

is many things to many people,
but if you have the courage
to be true to yourself, to live up to your potential,
to be fair with others,
and always look for the good
in any situation...
Then you will have been the best
you can be, and there's no greater
success than that.

Linda Lee Elrod

Dedicated to all my family members and close friends.....

Life is precious! July 28, 1993

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An Ion-Neutral Complex Intermediate for Loss of Water from Fatty Acid

Carboxylates

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