STUDIES ON SOME CYCLIC CARBONYI COMPOUNDS CONTAINING SULFUR

A Thesis Submitted by

Mohamed Ibrahim Hegab Abdel-Aziz B. Sc. 1987, M. Sc. 1994

the Degree of Ph.D. in Organic Chemistry

under Supervisors

Dept. of Applied Chemistry Tech. Univ. of Denmark Lyngby, Denmark

Prof. Dr. A. Senning

Prof. Dr. F. A. Gad National Research Centre

Photochemistry Department Dokki, Giza, Egypt

Ain Shams University Faculty of Science Chemistry Department

1998

Prof. Dr. S. A. Shiba

Chemistry Department Faculty of Science Ain Shams University Abassia, Cairo, Egypt

Prof. Dr. F. M. Abdel-Megeid

Photochemistry Department National Research Centre Dokki, Giza, Egypt



STUDIES ON SOME CYCLIC CARBONYL COMPOUNDS CONTAINING SULFUR

presented By

Mohamed Ibrahim Hegab Abdel-Aziz

(B. Sc. And M. Sc. In chemistry)

Thesis Advisors

Prof. Dr. S. A. Shiba

Prof. Dr. Alexander Senning

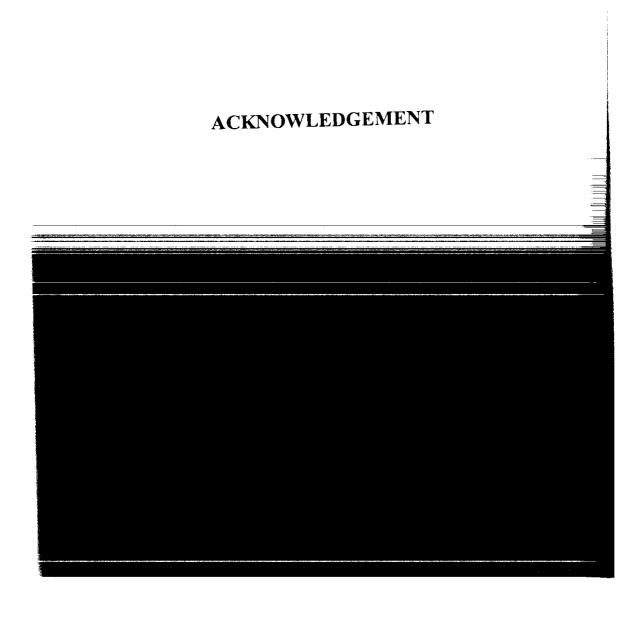
Prof. Dr. F. M. E. Abdel-Megeid

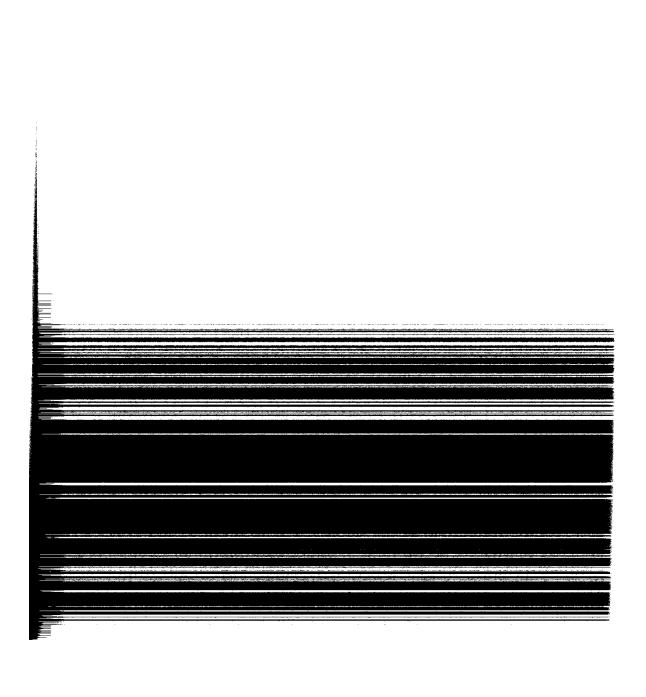
Prof. Dr. F. A. Gad

Thesis Approved

Head Of Chemistry Department

Prof. Dr. A. F. M. Fahmy





Acknowledgements

A grant from the Egyptain Government under the channel systems to the author is gratefully acknowledged.

Professor Sayed A. Shiba for his encouragement and his great help. Also he would like to thank Professor Alexander Senning for many useful discussions and a positive attitude to follow the progress of the work with keen interest, helpful guidance and valuable criticism which helped shape this thesis in its present form. Also he would like to thank Professor Farouk M. E. Abdel-Megeid for his helpful supervision and pursuance during this work. The author expresses his thanks to Professor Farouk A. Gad for his generous help and valuable advice.

The author expresses his sincere gratitude for the hospitality of the Department of Applied Chemistry (head: Professor U. Nissen) during the author's stay in Lyngby, Denmark.

The author would like to thank all the other Lyngby professors, especially Irene Shim, Knud Elming and Ib Jensen, also the author would like to thank all the technical staff, especially Jørn Nielsen and Betina Sørensen.

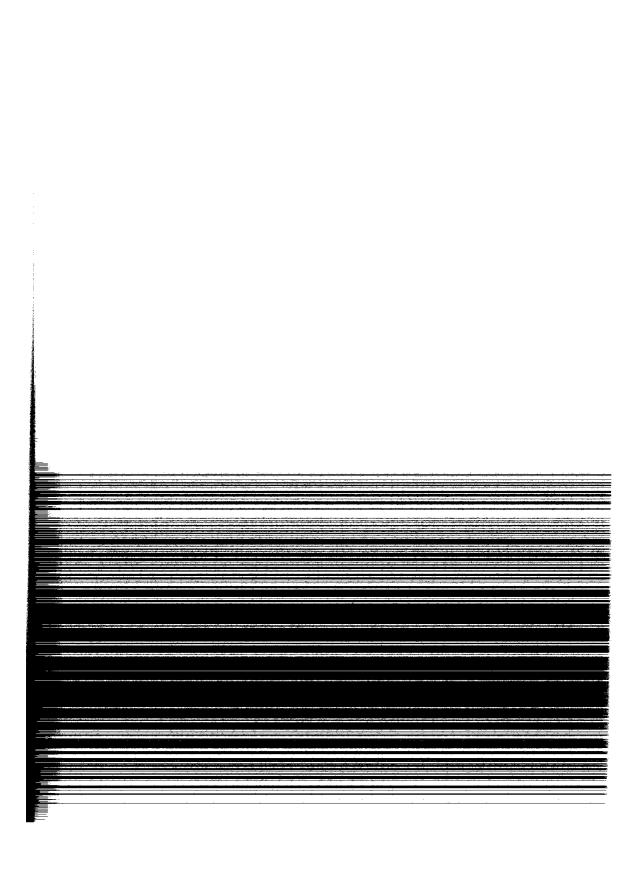
It would be impossible to mention all the people who have made these two years of stay at the Technical University of Denmark a memorable and valuable part of the author's studies.

Professor Jørgen Møller of Odense University was most helpful with the recording and interpretation of specially demanding mass spectrometric data. Professor Inger Søtofte carried out a number of X-ray crystallographic structure determinations which were extremely useful for the progress of the author's work. Mrs. Jytte Grove-Rasmussen was most cooperative in the recording of a large number of NMR spectra.

Mohamed Ibrahim Hegab Abdel-Aziz



CONTENTS



CONTENTS

	i
LIST OF FIGURES	ii
LIST OF TABLES	1
SUMMARY	4
INTRODUCTION	4
1. THE CHEMISTRY OF SULFENYL CHLORIDES	•
1.1. Synthesis of sulfenyl chlorides	4
1.1.1. Alkane- and arenesulfenyl chlorides	4
1.1.1.1. Chlorination of organic disulfides	4
1.1.1.2. Chlorination of thiols	4
1.1.1.3. Chlorination of sulfides	4
1.1.1.4. Chlorination of thiocarbonyl	
compounds	5
1.1.1.5. Application of sulfur dichloride	7
1.1.2. Alkane- and arenesulfenyl chlorides bearing	
otherfunctional groups in the molecule	7
1.1.2.1. Oxo sulfenyl chlorides	7
1.1.2.2. Cyano sulfenyl chlorides	15
1.1.2.3. Iminomethanesulfenyl chlorides a	ınd
related compounds	16
1.1.3. Acyl sulfenyl chlorides and related	
compounds	16
1.1.3.1. Chlorination of diacyl sulfides	16
1.1.3.2. Chlorination of O-trimethylsilyl	
thiocarboxylates	17
1.1.3.3.Chlorination of thiocarboxylic	
acids	17
1.1.3.4. Chlorination of diphenyltin bis-	
thiocarboxylates	17
1.1.4. Amino sulfenyl chlorides	18
1.1.4. Amino sugenti chio idea	

1.1.4.1. Amino sulfenyl chlorides via	
chlorination of bis-amino disul-	fides18
1.1.4.2. Sulfur dichloride procedure	18
1.1.4.3. Other methods	19
1.1.5. Phosphoranesulfenyl chlorides	19
1.1.5.1. Oxophosphoranesulfenyl chloric	les 19
1.1.5.2. Thioxophosphoranesulfenyl	
chlorides	21
1.1.6. Silanesulfenyl chlorides	22
1.1.7. Thiosulfenyl chlorides	22
1.1.7.1. Chlorolysis of acyl disulfides	22
1.1.7.2. Reaction of thiols with sulfur	
dichloride	23
1.1.7.3. Reaction of sulfur dichloride wit	h
thiocarbonyl compounds	23
1.1.7.4. Insertion of sulfur into the S-Cl	
bond	23
1.1.7.5. Disulfur dichloride procedures	24
1.2. Reactions of sulfenyl chlorides	25
1.2.1. Reactions with N-nucleophiles	25
1.2.1.1. Reactions with nitrogen	
nucleophiles	25
1.2.1.2. Reactions with acohols	25
1.2.1.3. Reactions with thiols	25
1.2.2. Reactions with π -nucleophiles	26
1.2.2.1. Reaction with arenes and enols	26
1.2.2.2. Reaction with alkenes	26
2. THE CHEMISTRY OF THIONE S-IMIDES	27
2.1. Structure and spectral properties	27
2.2. Syntheses	29
2.2.1. Nucleophilic substitution of sulforium ions	29

2.2.1.1. Reaction of thiones with	
N-CHOIOaimacs	29
2.2.1.2. Reaction of thiones with bromine	
and sulfonamides in the presence	
of triethylamine	29
2.2.1.3. Reaction of thiones with chloramin	e
salts	31
2.2.2. 1,3-Elimination from substituted	
sulfenamides	32
2.2.2.1. Dehydrochlorination of an	
N-benzoyl-α-chloro-sulfenamide v	vith
triethylamine	32
2.2.2.2. Dehydrohalogenation of a sulfen-	
amide with sodium hexamethyldi-	
silazanide	33
2.2.2.3. Dehydrochlorination of N-(p-tolyl)-
trichloromethanesulfenamide wit	
potassium hydroxide	34
2.2.2.4. Reaction of α -chloro sulfenyl	
chlorides with tert-butylamine	35
2.2.3. 1,2-Elimination from substituted sulfilimines	: 36
2.2.4. Conversion of N-sulfinylamines into thione	
S-imides	37
2.2.4.1. Wittig-type reactions of phosphot	anes
with N-sulfinyl-p-toluensulfon	
	37
2.2.4.2. Alkylidenation of N-sulfenylamit	nes
with α-silyl carbanions	39
2.2.5. Conversion of sulfines into thione S-imides	39
2.3. The chemical properties of the thione S-imides	40
2.3.1. Reactions with nucleophiles	40

2.3.1.1. Reactions with carbanions	40
2.3.1.2. Reactions with amines	4
2.3.1.3. Reactions with thiols	42
2.3.1.4. Reactions with halide anions	42
2.3.1.5. Reaction with phosphines	43
2.3.2. Thermolysis	43
2.3.3. Reactions with electrophiles	44
2.3.3.1. Reactions with acyl halides	44
2.3.3.2. Reactions with protic acids	46
2.3.3.3. Reaction with carbonium ions	46
2.3.4. Photoreactions	47
2.3.5. Cycloadditions and related reactions	47
2.3.5.1. Reactions with carbon-carbon do	ouble
bonds	48
2.3.5.2. Reactions with carbon-hetero ato	m
double bonds	51
2.3.5.3. Reactions with heterocunulenes	51
2.3.6. Reactions with organometallics	53
3. THIOSULFINES	54
DISCUSSION	57
LIST OF NEW COMPOUNDS	94
EXPERIMENTAL	98
REFERENCES	151
	121