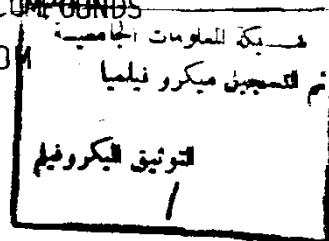


STUDIES ON SOME HETEROCYCLIC COMPOUNDS
WHICH CONTAIN NITROGEN ATOM



A THESIS

Submitted By

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To

Faculty of Science

Ain Shams University

503593
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For The Degree of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY

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CAIRO

1993

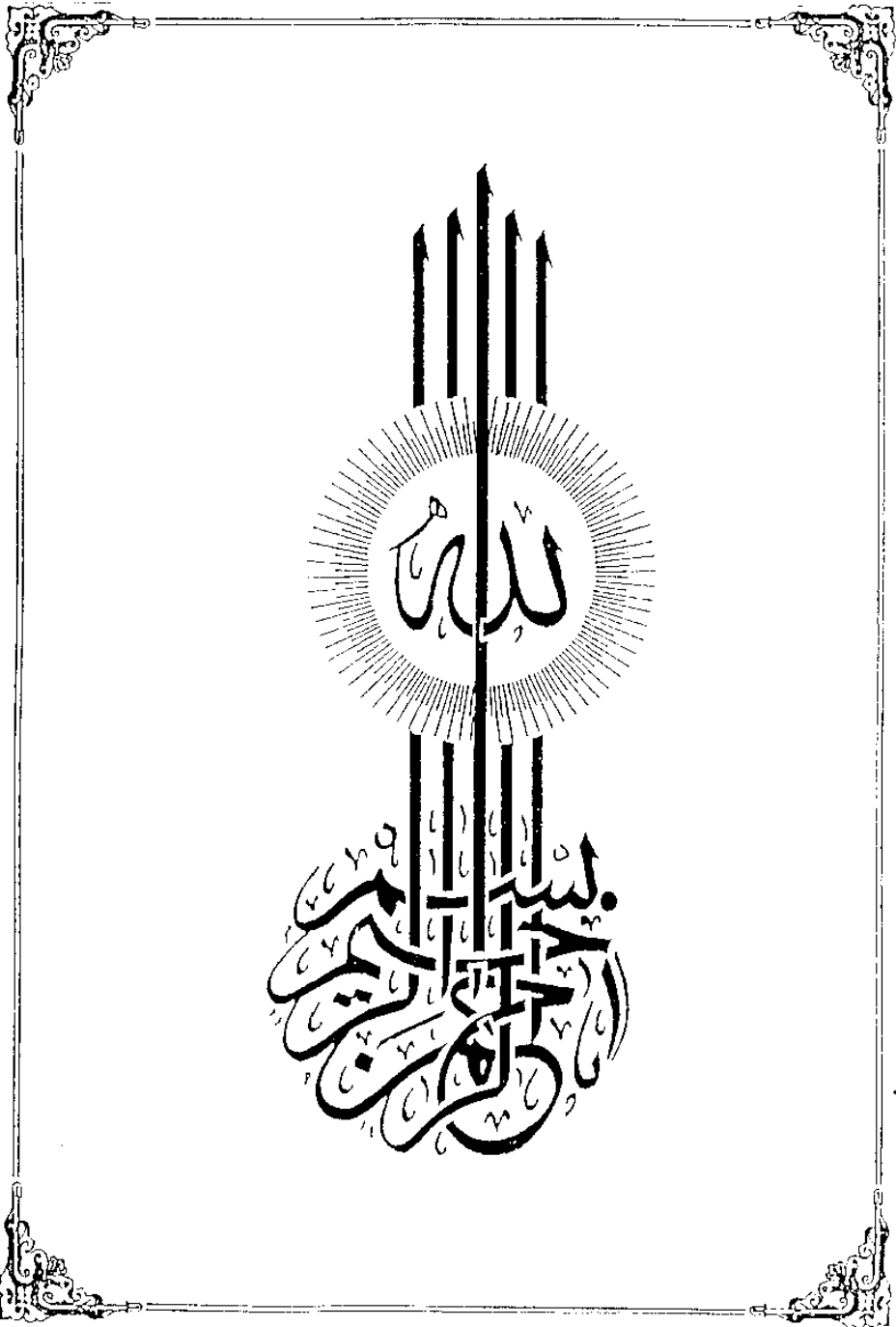


بسم الله الرحمن الرحيم

"وَقُلْ رَبِّ زِدْنِي عِلْمًا."

صدق الله العظيم

سورة طه - آية ١١٤



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ACKNOWLEDGEMENT

The author is very grateful to Prof. Dr. Gamal El-Din M. Mousssa (Late), Professor of Organic Chemistry, Faculty of Science, Ain Shams University, for indispensable advice, continuous encouragement and for his valuable help.

The author also wishes to express her deep thanks and sincere gratitude to Dr. Ali M. Youssef, Assistant Professor of Organic Chemistry, Faculty of Science, Ain Shams University, for suggesting the problem, continual advice, valuable discussion and criticism during the course of this work.

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Summary

S U M M A R Y

(i)

The first part comprises the mode of addition of some nucleophiles having two different nucleophilic centres to benzoylisocyanate. So ethanolamine, ethanolthiol and α -amino-thiophenol were added in equimolar ratio to benzoylisothiocyanate. It was established that the more nucleophile group attacked the C=S group. So in case of the addition of ethanolamine the attacking nucleophile was NH_2 , whereas, on the addition of ethanolthiol the SH group was the attacking species. Further, in case of the aromatic bifunctional nucleophile " α -amino-thiophenol," the SH group also added to the electrophile C=S and the products I, II, III were obtained respectively. From the spectral data, it was concluded the former result, and appearance of stretching vibrations relative to OH, OH and NH_2 groups respectively realises that observation. The newly synthesized thiocarbamid acid derivatives (I, II, III) were established by using analytical as well as spectroscopic tools.

The second part of this thesis deals with the introducing dimethylsilylene group $(\text{CH}_3)_2\text{Si} <$ to different compounds having two acidic hydrogen with elimination of 2 moles of HCl on reaction with dichlorodimethylsilylane to prepare cyclopentane ring (IV) upon reaction with diol. The mono-phenylhydrazine of benzoin or its derivative reacts with dichlorodimethylsilylane to produce silica cyclohexane derivatives (V, VI), the reaction temperature must be taken into consideration,

that at lower temperature, firstly the Si-O bond is formed, whereas at higher temperature the Si-N bond will be formed and six membered ring is being obtained. The diphenylhydrazone of benzil and its derivative reacted with dichlorodimethylsilane to produce the sila cycloheptanes (VII, VIII). The optimum structure of the prepared five, six and seven membered rings were studied using MM-2, molecular force field method, **ALKEMY II programme**, from which the configuration of the molecules were detected Figs. (2-4). The reaction between the active chlorine on silicon in case of dichlorodimethylsilane leads us to investigate the reaction between 1,1-dichloro-1,1,3,3-tetramethyldisiloxane (94) and diaryl thiocarbaniide derivatives. It was found that the reaction undergone between the chlorine atom on the silicon and only one N-H (acidic) hydrogen leaving the other N-H of the thiocarbaniide. The remaining chlorine of the siloxane reacted with another thiocarbaniide molecule, the thiocarbaniide disiloxanes (IX - XIII) prepared were found to have an open structures i.e. Ph-N-C-N-Ph and $\text{CH}_3\text{-Si-O-Si-CH}_3$ (97) and no cyclic structures were obtained (96). These results were substantiated from analytical and spectral data using infrared spectroscopy and $^1\text{H-NMR}$ patterns, which revealed the presence of free NH in all prepared compounds in this series. The investigations by molecular force field method using **ALKEMY II programme** showed the optimum configurations of this series Fig. (5). From this study, it was observed that the two methyl groups on the silicon atoms-A and B (94) are not identical

(ii)

in their configuration inspite of the tetrahedral structure of silicon atom, thus one of them is embeded in the aromatic ring which give a good reason for the difference in the observed chemical shifts of protons in both methyl groups which was also clearly observed in $^1\text{H-NMR}$ spectral data of these compounds. Tables (26-30).

(iii)

Introduction