STUDIES ON SOME HETEROCYCLIC COMPOUNDS WHICH CONTAIN NITROGEN ATOM

A THESIS

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بسم الله الرحمن الرحيم

" وقل ربِّ زدني علماً . "

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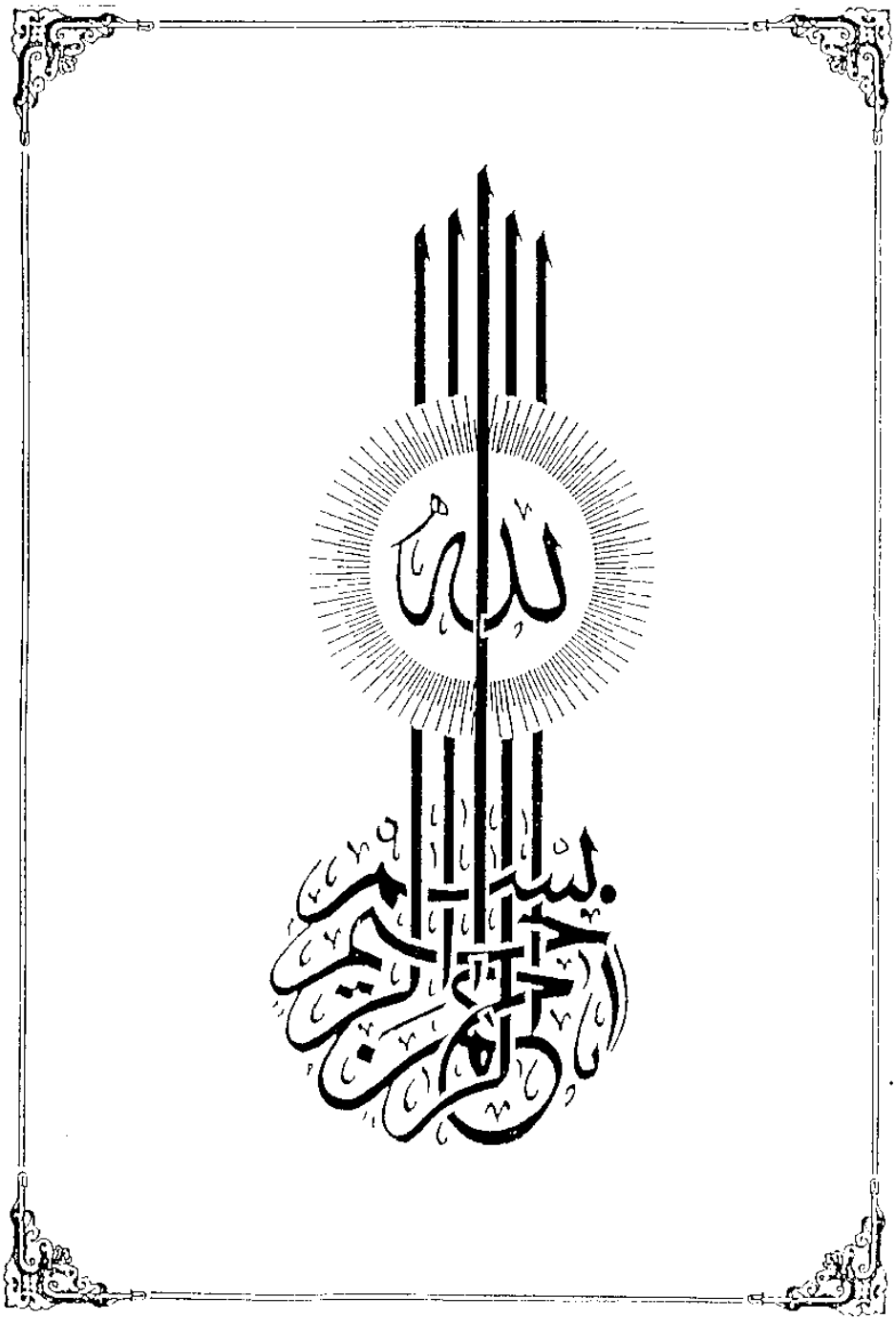

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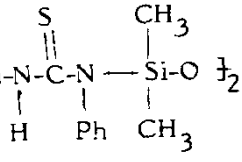
SUMMARY

The first part comprises the mode of addition of some nucleophiles having two different nucleophilic centres to benzoylisocyanate. So ethanolamine, ethanolthiol and o-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 $\ddot{N}H_2$, whereas, on the addition of ethanolthiole the SH group was the attacking species. Further, in case of the aromatic bifunctional nucelophile "o-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 thiocarbamic 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 $(CH_3)_2Si<$ to different compounds having two acidic hydrogen with elimination of 2 moles of HCl on reaction with dichlorodimethylsilane to prepare cyclopentane ring (IV) upon reaction with diole. The mono-phenylhydrazine of benzoin or its derivative reacts with dichlorodimethylsilane to produce sila 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 thiocarbanilide 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 thiocarbanilide. The remaining chlorine of the siloxane reacted with another thiocarbanilide molecule, the thiocarbanilide disiloxanes **(IX - XIII)** prepared were found to have an open structures i.e.  **(97)** and no cyclic structures were obtained **(96)**. These results were substantiated from analytical and spectral data using infrared spectroscopy and ^{1}H-NMR patterns, which reviled 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

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}H-NMR spectral data of these compounds. Tables (26-30).

Introduction