synthesis and spectral studies on some biologically active nitrogen heterocycles

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The present work in this thesis is arranged in three parts, Part (I)Fristly, in this part we prepared the two heterocyclic compounds benzotriazine-3-thione and benzimidazole-2-thione according to literature. But we found all analysis data the same structure for the two compounds this led to us to confirm this result anylsis data by used reacted with different glycosyl halides to give us S-and N-glycosides respectivelly, for the benzimidazole-2-thione only this indicate the benzotriazine structure not right in the literature.The synthesis of benzimidazole-2-thone 157 was prepared by treament of O-phenylene diamine 155 with thiosemicarbazide cyclized by fussion after one hour. Similarly reaction of O-phenylene diamine 155 with thiourea gave the same product. Also, the reaction of O-phenylene diamine 155 with carbon disulfide in presence of potassium hydroxide in ethanol gave the benzimidazole-2-thione 157 the same product (Scheme 1).When benzimidazole-2-thione 157 was reacted with the acetylated glucosyl bromide 158a and acetylated galactosyl bromide 158b as well as benzoylated glucosyl bromide 158c and 2-N-acetyl-amino glucosyl chloride 158d, the resulting products were found to be dependent on the used acid scavengers. In presence of K2CO3 in acetone, the respective thioglycosides 161a and 161b, but not 159a and 159b, were obtained and were accompanied by minor products 162a and 162b, but not 160a and 160b. On the other hand, 161c and 161d were not accompanied by minor products. When triethylamine or potassium hydroxide were used as the scavengers, the products were only of the thioglycoside type 161a-d (Scheme 2).Part (II)The second part deals with the synthesis of enaminone derivatives 165a-cwere prepared by the reaction of dimedone 163 with aniline derivatives 164a-c in the presence of acetic acid and reflux for 6h., afforded enaminone derivatives (Scheme 3).The reaction of enaminone derivatives 165a-c with carbon disulfide in the presence of sodium hydroxide in dimethyl sulfoxide (DMSO) was formed intermediate 166a-c, followed by alkylation with n-butyl bromide at r.t., gave the corresponding enamino dithiocarboxylates 167a-c, while the reaction of the intermediate 166a-c, with carbon disulfide in the presence of sodium hydroxide in dimethyl sulfoxide at r.t., and of n-butyl bromide was added to reaction mixture gave benzothiazine derivatives 168 a-c.By the same way the reaction of enaminone dervatives 165a-c, with 1-bromoundecane, bromoethanol and benzyl bromide gave the corresponding enamino dithiocarboxylates 169-171(a-c), respectively (Scheme 5).Also, the reaction of enaminones derivatives 165a-c, with α-aceto bromoglucose and α-aceto

-bromogalactose afforded (2′,3′,4′,6′-tetra-O-acetyl-ß-D glucopyranosyl)[2-(arylamino)-4,4-dimethyl-6-oxocyclohex-1-ene]carbodithioates -172a-c, and (2′,3′,4′,6′-tetra-O-acetyl-ß-D galactopyranosyl)[2-(arylamino)-4,4-dimethyl-6-oxocyclohex-1-ene]carbodithioates 173a-c, respectively.While, the excess of carbon disulfide and sodium hydroxide were used to cyclize the product benzothiazine derivatives from acetylated glycosyl halides 174a-c was not obtained (Scheme 6). Finally, the compound of2-(2,4-dichlor ophenylamino)-6-hdrazono-4,4-dimethylcyclohex-1-enecarbothiohydrazide as intermediate 175 was prepared by the reaction of benzyl-2-(2,4-dichlorophenylamin o)-5,5-dimethyl-3-oxo-cyclohex-1-enecarbodithioate 171a with hydrazine hydrate in the presence of ethanol in boiling solution. Followed direct by the refluxing with acetone afforded the 6,6-dimethyl-4-(2-(propan-2-ylidene)hydrazinyl)-6,7-dihydro-2H-idazole-3(5H)-thione -176 (Scheme 7).Part (III)The third part deals with the alkylation of 5-amino thiadiazole-2-thone 177 in the presence of potassum carbonate in acetone afordded the intermediate 178 followed by the reaction with different types of alkylating agents like Bromoethanol, chloropropanol, chloropropan-2-ol, 2-bromo-1,1-diethoxyethane, 1-bromoundecane, ethyl chloroacetate, 1-chloro -acetonitrile, 1-chloroacetic acid, n-butyl bromide and benzyl bromide to give S alkylation of 5-amino- thiadiazole-2-thone 179a-j, respectively (Scheme 8).Moreover the reaction of 5-amino-thiadiazole-2-thone 177 with α-acetobromoglucose afforded two products S-glucosides 180 and 181 one of them having free group NH2 and another one is NHAc group, similarly the same result with α-acetobromogalactose and 2-N-acetylaminoglucosyl chloride afforded thioglycoside derivatives free NH2 and thioglycoside derivatives having NHAc group 182-185 respectively,On the other -hand, the reaction of compound 177 with benzoyl bromoglucose afforded S glucoside derivative 186 in addition to the N-glucoside derivative 187. Finally the acetylation of 180 and 186 with acetic anhydride in presence of dry pyridine afforded 181 and 188 in good yield (Scheme 9).