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STUDIES ON THE AZIDOAZOMETHINE-TETRAZOLE EQUILIBRIUM

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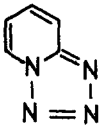
α -Azido-substituted,nitrogen containing heterocycles (Ia) may be considered as existing in a tautomeric equilibrium with the corresponding fused-ring tetrazolo forms (Ib).

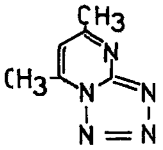
(Ia) (Ib)

In the solid state compounds I exist mainly in the tetrazole form (Ib) since their I.R. and U.V. spectra are usually lacking the absorption bands assigned to the azide function (1). These bands may instead be present when compounds I are examined in solution,their intensity depending on the nature of the solvent,on temperature and on characteristics of the heterocyclic ring. In some cases separation of the two species was achieved by paper chromatography of their ethanolic solutions (1) and more recently the equilibrium has been studied in quantitative form for 4,6-dimethyl,2-azidopyrimidine with the aid of N.M.R. techniques (2).

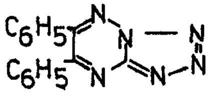
The aim of this work has been to study the azidoazomethine-tetrazole equilibrium from a chemical point of view through the investigation of the reaction of some compounds of general formula I with an enamine derivative (°). The following compounds have been examined : tetrazolo [5,1-a] pyridine (II)(4); 5,7-dimethyl-tetrazolo [1,5-a] pyrimidine (III)(5); 5,6-diphenyl-tetrazolo [1,5-b] as.triazine (IV)(°°) and tetrazolo [5,1-b] benzothiazole (V)(7).



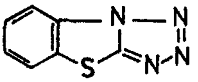
(II)



(III)



(IV)

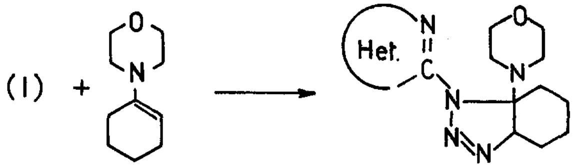


(V)

(°)- The reaction of enamines with aryl- and acyl-azides has been widely investigated in this laboratory in recent years (3).

(°°)- M.P. 198° (acetic acid). Obtained by treatment of 3-hydrazino,5,6-diphenyl as.triazine (6) with nitrous acid.

Spectrophotometrical measurements carried out on these compounds in the solid state are in agreement with the tetrazole structures. Existence of the reactive tautomeric azide forms has however been confirmed by the results of the reaction of tetrazoles II,III, IV and V with α-cyclohexene-N-morpholine (VI) which furnished the corresponding addition compounds (general formula VII). Observed reactivity was in the following order : V > IV ≃ III > II.



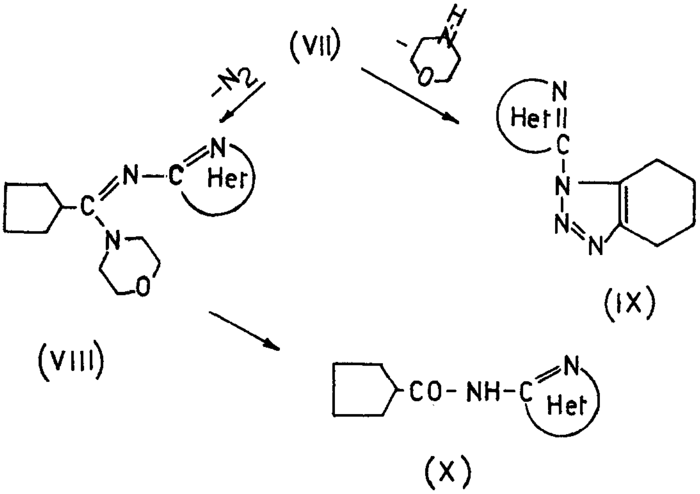
(VI) (VII)

Data related to adducts VII have been assembled in TABLE 1.

TABLE 1

Het. (VII)	M.P.	Yield	C%		H%		N%	
			C.	F.	C.	F.	C.	F.
α-Pyridino-	99°	46%	62,71	62,80	7,31	7,62	24,39	24,60
4,6-dimethyl-2-pyrimidino-	111°	60%	60,75	60,67	7,59	7,75	26,58	26,99
5,6-diphenyl-3-as.triazino-	138°	40%	68,02	67,80	6,12	6,29	22,22	22,35
2-benzothiazole-	86°	90%	59,47	59,00	6,12	6,14	20,40	20,00

The structures of the four compounds represented by general formula VII were confirmed by rearrangement to the corresponding substituted cyclopentancarbonyl-ammidines (VIII)(by heat or by strong acids) (3) and by conversion into the corresponding 1-substituted-4-5-cyclotetramethylene-1,2,3-triazoles (IX)(by alkalies) (3). From compound VII (Het. = 5,6-diphenyl,3-as.triazino) the corresponding ammidine VIII was obtained on heating in dioxane solution. M.P. 128° (ethanol). Found C = 71,60% , H = 6,35 , N = 17,00 . Calculated : C = 72,63% , H = 6,53% , N = 16,94% .



Other ammidines of general formula VIII were not isolated but directly converted by hydrolytic cleavage into the corresponding cyclopentancarbamides (X). Treatment with alcoholic sodium hydroxide of compound VII (Het. = 2-benzothiazolo-)yielded the corresponding 1,2,3-triazole (IX) M.P. 146° (ethanol). Found C = 61,05% , H = 4,90% , N = 21,90% . Calculated for $C_{13}H_{12}N_4S$: C = 60,93% , H = 4,68% , N = 21,87% . The structure of the substituted triazoles IX was confirmed by alcoholysis with sodium ethoxide yielding 4,5-cyclotetramethylene-1,2,3-triazole (3) and the α-ethoxy-heterocycles.

Full details on this research will be published in subsequent papers.

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