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AZA-TRANSFER REACTIONS BETWEEN SOME HETEROCYCLIC HYDRAZINO COMPOUNDS AND BENZENEDIAZONIUM TETRAFLUOROBORATE OR 3-DIAZOINDAZOLE

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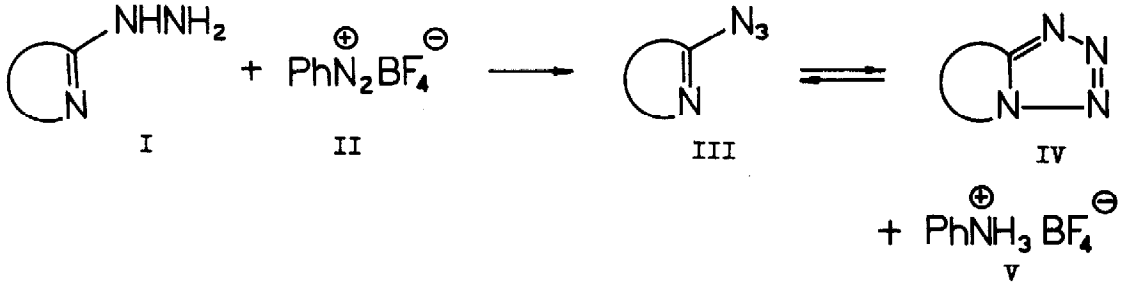
In the reactions so far investigated between aromatic diazonium salts and aryl- and alkyl-hydrazines besides the anticipated tetrazenes, always aromatic azides were formed [1]. Recently the reduction of 3-diazoindazole into 3-hydrazinoindazole, giving indazole, 3-aminoindazole and 3-azidoindazole as by-products, has been explained as to proceed via the corresponding tetrazene and triazene intermediates [2].

In this communication we wish to report the reaction between some heterocyclic hydrazino compounds and benzenediazonium tetrafluoroborate or 3-diazoindazole. The reaction between heterocyclic hydrazino compounds and benzenediazonium tetrafluoroborate takes place in methanol at room temperature in 5-10 minutes and involves a nitrogen atom transfer from benzenediazonium salt (II) to the heterocyclic hydrazino compound (I) to give either a heterocyclic azido compound (III) or tetrazoloazine (IV) and anilinium tetrafluoroborate (V) in almost quantitative yield. Table I.



I II III IV

V

On the other hand, the reactions between 3-diazoindazole (VI) and some heterocyclic hydrazino compounds (VII) are more complex. In these transformations a nitrogen atom is transferred either from 3-diazoindazole (VI) to the heterocyclic hydrazino compound (VII) affording 3-aminoindazole (IX) and the

Table I

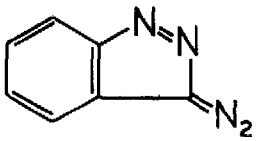
Starting compound (I)	Products (III) and/or (IV)[a]
2-hydrazinopyridine	tetrazolo/1,5-a/pyridine (3)
2-hydrazinopyridazine	tetrazolo/1,5-b/pyridazine (4)
2-hydrazinopyrazine	tetrazolo/1,5-a/pyrazine (5)
2-hydrazinopyrimidine	tetrazolo/1,5-a/pyrimidine + 2-azidopyrimidine (6)
6-hydrazinoimidazo/1,2-b/pyridazine	6-azidoimidazo/1,2-b/pyridazine (7)
2-hydrazinopyrido/1,2-a/pyrimid-4-one	2-azidopyrido/1,2-a/pyrimid-4-one (8)

a) The compounds are identical in all respects with the authentic samples prepared according to the procedures reported in the literature.

heterocyclic azide (XIII), or from heterocyclic hydrazine (VII) giving 3-azidoindazole (X) and the corresponding amine (XII). In all cases as by-products the parent systems,i.e. indazole (VIII) and the corresponding heterocycle (XI) are also formed.

To a stirred solution of 3-chloro-6-hydrazinopyridazine [9] (VIIa) in methanol an equivalent amount of 3-diazoindazole [10] (VI) was added in small portions. After standing for one hour at room temperature the reaction mixture was separated by t.l.c. The following products were isolated: indazole[11] (VIII, 5%), 3-aminoindazole[12] (IX, 16%), 3-azidoindazole [2] (X, 3%), 3-amino-6-chloropyridazine [13] (XIIa, 4%), 6-chlorotetrazolo/1,5-b/pyridazine [14] (XIV, R=Cl,7%) as the stable isomer of XIIIa and 6-methoxytetrazolo/1,5-b/pyridazine [14] (XIV, R=OCH_3,2%). The latter compound was formed from 6-chlorotetrazolo/1,5-b/pyridazine (XIV, R=Cl) during work-up procedure.

In a similar experiment between 6-hydrazinotetrazolo/1,5-b/pyridazine[15] (VIIb) and 3-diazoindazole [10] (VI) in ethanol the following products were separated and identified: indazole [11] (VIII,16%), tetrazolo/1,5-b/pyridazine[4] (XIb, 4%) and 6-azidotetrazolo/1,5-b/pyridazine [15] (XIIIb, 8%). Reaction of 3-diazoindazole [10] (VI) with 6-hydrazino-s-triazolo/4,3-b/pyridazine [4](VIIc) afforded a mixture of s-triazolo/4,3-b/pyridazine [4] (XIc,10%) and indazole[11](VIII, 31%). 3-Diazoindazole[10] (VI) and 6-hydrazino-s-triazolo/1,5-b/pyridazine [16] (VIId) yielded indazole [11] (VIII,16%) and 6-azido-s-triazolo/1,5-b/pyridazine[16](XIIId, 3%). Separation of the reaction mixture of 3-diazoindazole [10] (VI) and 6-hydrazinoimidazo/1,2-b/pyridazine [7] (VIIe) gave 3-aminoindazole [12] (IX, 31%), indazole[11](VIII,3%), imidazo/1,2-b)pyridazine[17] (XIe,1%) and 6-azidoimidazo/1,2-b/pyridazine [7] (XIIIe, 23%). From 3-diazoindazole[10] (VI) and 2-hydrazinopyrido /1,2-a/pyrimid-4-one [18](VIIf) indazole [11](VIII,34%),2-aminopyrido/1,2-a/pyrimid-4-one[19] (XIIf, 4,5%),3-aminoindazole[12] (IX,3%)and 2-azidopyrido/1,2-a/pyrimid-4-one[18] (XIIIf, 10%) were isolated.



VI

+ H_2NHN-R_1

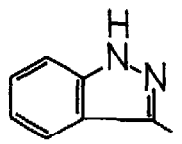
VII

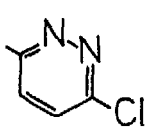
$R-H$ + $R-NH_2$ + $R-N_3$

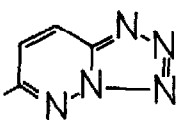
VIII IX X

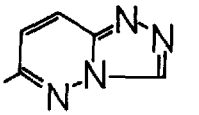
+ $H-R_1$ + H_2N-R_1 + N_3-R_1

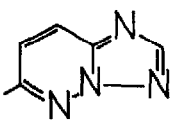
XI XII XIII

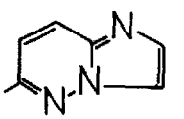
R= 

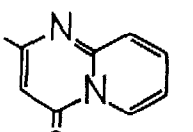
R_1= 

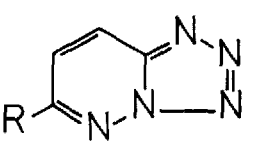
a 

b 

c 

d 

e 

f 

XIV

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19.) The compound was identical in all respects with an authentic sample prepared from 2-azidopyrido/1,2-a/pyrimid-4-one by reduction with H_2S, m.p. 25o-255°