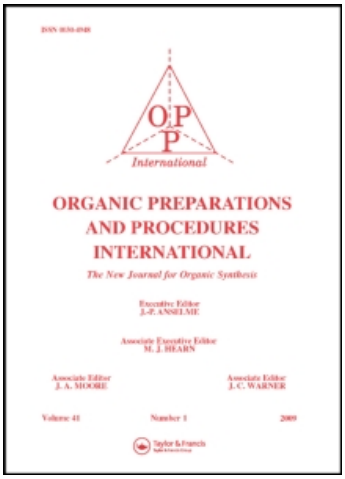

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A NOVEL METHOD FOR THE PREPARATION OF SUBSTITUTED 5-AMINO-1,2,3,4-THIATRIAZOLES BY AZA TRANSFER REACTION

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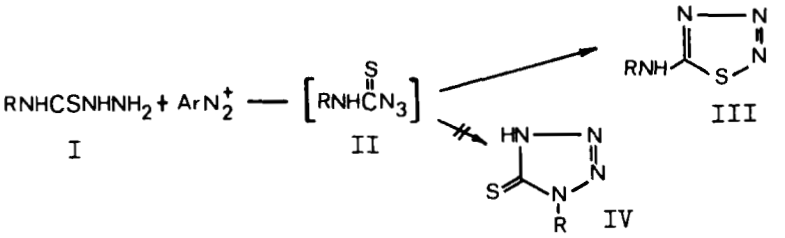
Recently, we have found that the reaction between heterocyclic hydrazino compounds and benzenediazonium tetrafluoroborate involves a nitrogen atom transfer to give heterocyclic azido compounds or tetrazoloazines and anilinium tetrafluoroborate in almost quantitative yield.[1] The reaction between heterocyclic diazo compounds and aliphatic, aromatic or heterocyclic hydrazines is more complex and a mixture of different products is formed.[2] On the other hand, it was found that the reaction between thiophenol and heterocyclic diazo compounds resulted in the formation of the corresponding diazosulfides.[3] In view of these findings, it seemed of interest to investigate the reaction between thiosemicarbazide or 4-substituted thiosemicarbazides and diazonium salts under the conditions of aza transfer.

We now report that the reaction between thiosemicarbazides (I) and benzenediazonium tetrafluoroborate or diazotized sulfanilic acid gives only one type of products which were identified as substituted 5-amino-1,2,3,4-thiatriazoles(III) (Table I). No isomerization into 1-substituted tetrazoline-

-5(4H)thiones (IV) under the reaction conditions employed



could be observed. This novel aza transfer reaction represents an efficient method for the preparation of substituted 5-amino-1,2,3,4-thiatriazoles[4] and is more advantageous than the nitrosation procedure since it proceeds under almost neutral reaction conditions.

Table I. N-Substituted 5-amino-1,2,3,4-thiatriazoles (III)

R	Yields(%)[a] Procedure A	Procedure B	mp. (°C)	Reference[b]
H		35	130-132	5,6
Methyl	56	55	94	6,7
Benzyl	52	70	78-80	8
Cyclohexyl	64	60	113-115	9
Phenyl	61	65	145-147	8,10,11
o-Tolyl	71	63	109-111	8
m-Chlorophenyl	55	66	133-134	12
1-Naphthyl	50	37	128-130	c
2,4-Dimethylphenyl	41	31	110-112	12
o-Methoxyphenyl	54	66	90	8

a. Yields of purified products are given. TLC showed absence of any other products.

b. Infrared spectra of the compounds prepared were identical with those of authentic specimens.

c. Anal. Calcd. for $C_{11}H_8N_4S$: C, 57.89; H, 3.53; N, 24.55. Found: C, 58.24; H, 3.82; N 24.36.

EXPERIMENTAL [13]

General Procedures. Procedure A. - To a suspension of the thiosemicarbazide (0.5 mmole) in methanol (5 ml) was added benzenediazonium tetrafluoroborate (96 mg) and the reaction mixture was left at room temperature for 15 minutes. Methanol was removed in vacuo and water (5 ml) was added to the residue. The product was filtered and recrystallized from aqueous methanol.

Procedure B. - The procedure is essentially the same as that described above but diazotized sulfanilic acid was added (92.4 mg) and after 15 minutes sulfanilic acid was removed by filtration. Crushed ice (5 g) was added to the filtrate and the product was filtered and recrystallized as above.

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