BRIEF COMMUNICATIONS

UDC 547.79 + 542.952 + 549.959

THERMAL ISOMERIZATION OF 1-PHENYL-5-HYDRAZINOTETRAZOLE

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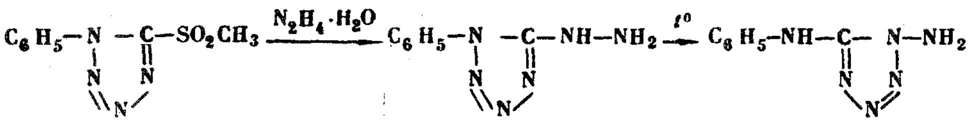
A new example of isomerization of a tetrazole derivative (1-phenyl-5-hydrazinotetrazole to 1-amino-5-anilinotetrazole) is described. A convenient method for preparing 1-phenyl-5-hydrazinotetrazole is described.

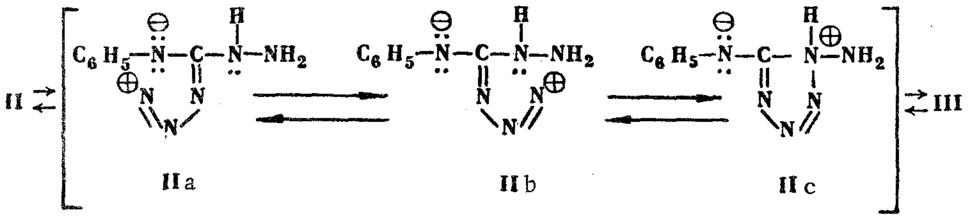
1-Phenyl-5-hydrazinotetrazole (II) was previously prepared [1] by reacting 1-phenyl-5-bromotetrazole with hydrazine hydrate. The hydrazine II (mp 140°) was here prepared by heating 1-phenyl-5-methylsulfonyltetrazole [2] with hydrazine hydrate for a short time, and the yield was almost quantitative. Prolonged refluxing of the sulfone I with hydrazine hydrate gives a crystalline substance mp 210°, which, according to its elementary analysis, is isomeric with the starting II. The same substance was obtained by boiling II in high-boiling solvents (xylene, morpholine, benzylamine). Taking into account data on the thermal isomerization of 1-phenyl-5-aminotetrazole to 5-anilinotetrazole [3], it could be assumed that under the experimental conditions 1-phenyl-5-hydrazinotetrazole underwent isomerization to 1-amino-5-anilinotetrazole (III)



I II III

This assumption was confirmed by comparing the isomerization product with the compound III of known structure, prepared by Stoll's method from 4-phenylthiosemicarbazide.

The mechanism of the reaction can be represented as follows: heterolytic splitting of the N^2-N^1 bond takes place on heating, with formation of an intermediate guanilazide (IIa $\rightleftarrows$ IIb), which recloses to the tetrazole at the nitrogen of the hydrazine group (IIc $\rightleftarrows$ III)



IIa IIb IIc

Obviously isomerization of hydrazine II to III is an equilibrium process, with a large shift of the equilibrium towards the side of the thermodynamically more stable amine III.

Experimental

Hydrazinolysis of 1-phenyl-5-methylsulfonyltetrazole. A mixture of 18.8 g (0.084 mole) sulfone I and 32 ml hydrazine hydrate was refluxed for 2-3 min. On cooling a precipitate of the hydrazine II separated, yield 14 g (95%), mp 136-137°, recrystallized from water mp 140-141° (the literature [1] gives 125°). Found: N 47.72%. Calculated for $C_7H_8N_6$: N 47.72%.

Isomerization of 1-phenyl-5-hydrazinotetrazole. 0.44 g (2.5 mmole) 1-phenyl-5-hydrazinotetrazole was refluxed in 35 ml xylene. On heating the hydrazine II first went into solution, and after 2-3 min a crystalline precipitate started to form. After cooling the mixture was filtered, and the solid washed with ether. Yield 0.4 g (91%), after recrystallizing from ethanol mp 210° (the literature [4] gives 210°). Found: C 47.76; H 4.75; N 48.31%. Calculated for $C_7H_8N_6$: C 47.72; H 4.56; N 47.72%.

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LETTERS TO THE EDITOR

UDC 547.855

SUBSTITUTED SPIRO [PYRAZOLO-4, 5'-PYRIMIDINES]

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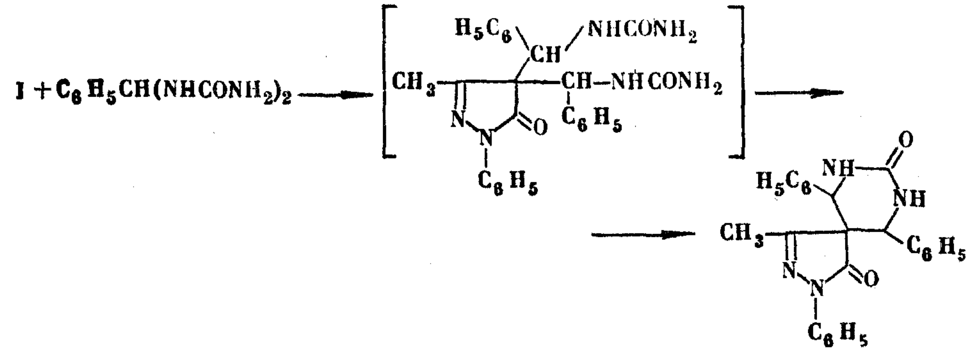
Continuing work on the reaction of arylidenebisureas with compounds containing the CH_2CO group, for the purpose of preparing pyrimidine derivatives [1], the reaction of benzalbisurea with 1-phenyl-3-methylpyrazolone-5 (I) has been investigated by the present authors. 1 mole I and 2 mole benzalbisurea in dry n-butanol (in the presence of HCl) at 100° gave an approximately 50% yield of a compound mp 237-239°. Its UV spectrum was similar to that of I; it was insoluble in alkalies, did not give a coloration with either ferric chloride or p-dimethylaminobenzaldehyde. When boiled with 10% NaOH the smell of benzaldehyde appears, and I and urea are found in solution (paper chromatography). The IR spectrum of the compound (in KBr) has an absorption band at 1680 cm^{-1}, which can be ascribed to vibrations of the CO group in urea, and an absorption band at 1703 cm^{-1}, characteristic of the CO group of 4, 4-disubstituted pyrazolones-5 [2]. The elementary analysis corresponds to a formula $C_{25}H_{22}N_4O_2$. From these results it can be inferred that the compound is 1, 4', 6'-triphenyl-3-methylspiro [pyrazolo-4, 5'-hexahydropyrimidine]-5, 2'-dione, and is a member of a new heterocyclic system. Its formation can be represented by the following equation:



Similarly, reaction of I with anisalbisurea gave 1-phenyl-4', 6'-bis (p-methoxyphenyl)-3-methylspiro [pyrazolo-4, 5'-hexahydropyrimidine]-5, 2'-dione, mp 200-204°.

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