

12 November 1964

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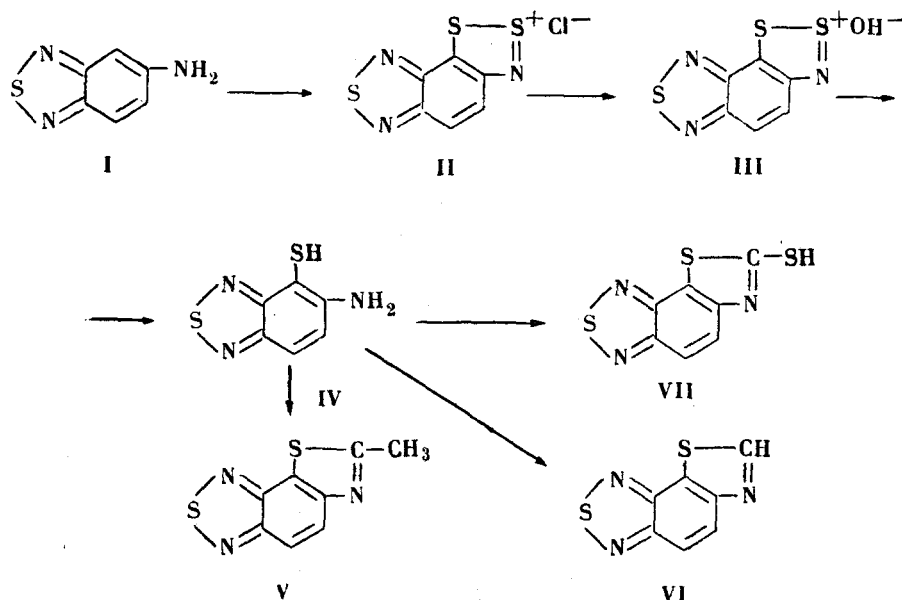
UDC 547.79+542.95

BEHAVIOR OF 4- AND 5- AMINOBENZ-2,1,3-THIADIAZOLES
UNDER HERZ AND SKRAUP REACTION CONDITIONS

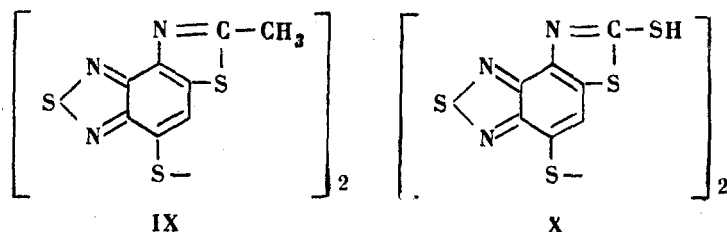
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Khimiya Geterotsiklicheskih Soedinenii, Vol. 1, No. 2, pp. 314-315, 1965

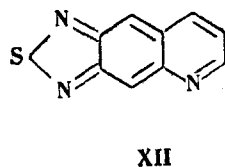
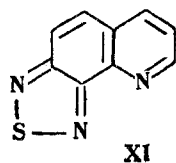
Like aromatic amines, 5-aminobenz-2,1,3-thiadiazole (I) reacts with sulfur chloride to give thiazothionium [5,4-e]benz-2,1,3-thiadiazole chloride (II), which, on treatment with water, gives the hydrate (III), mp 142-143° (from alcohol). Degradation of III with alcoholic alkali gives 5-amino-4-mercaptobenz-2,1,3-thiadiazole (IV), and the latter, treated with acetic anhydride, ethyl orthoformate, or carbon disulfide, gives 2-methylthiazolo[5,4-e]benz-2,1,3-thiadiazole (V), mp 137-139° (from alcohol), thiazolo[5,4-e]benz-2,1,3-thiadiazole (VI), mp 98-100° (from 50% alcohol), and 2-mercaptothiazolo[5,4-e]benz-2,1,3-thiadiazole (VII), mp 260-262° (decomp.), respectively.



When the above reactions are carried out with 4-aminobenz-2,1,3-thiadiazole (VIII), the end products, judging by the analytical data and certain properties, are 2-methylthiazolo[4,5-e]benz-2,1,3-thiadiazolyl-7-disulfide (IX), mp 266-270°, and 2-mercaptothiazolo[4,5-e]benz-2,1,3-thiadiazolyl-7-disulfide (X), mp 285-290°. The structures of the intermediates from which compounds IX and X are formed, are being investigated.



Reaction of 4-amino-(VIII) or 5-aminobenz-2,1,3-thiadiazoles (I) with glycerol, sulfuric and arsenic acids gives quinolino[7,8-d]-2,1,3-thiadiazole (XI), mp 139-140° (from petrol ether), and quinolino[6,7-d]2,1,3-thiadiazole (XII), mp 112-113° (from alcohol), respectively.



23 December 1964

Leningrad Chemical-Pharmaceutical Institute

UDC 547.856/78+542.95

HYDRAZINOLYSIS OF SOME QUINAZOLONES

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 315-316, 1965

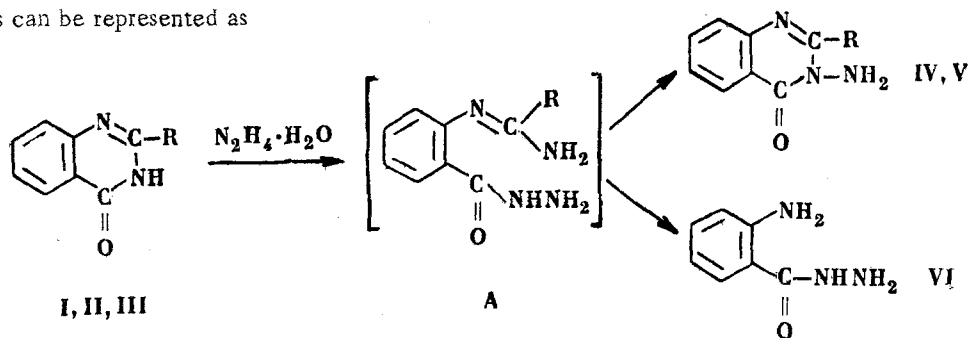
It is known that 2-aryl-3-arylamidoquinazol-4-ones undergo opening of the pyrimidine ring when heated with dilute aqueous alkali, giving substituted triazoles [1]. Not long ago the present authors [2] described a case of opening of the pyrimidine ring of 1-(2'-R-quinazolyl)-4-phenylthiosemicarbazides in acid medium. These facts, as well as a case of scission of pyrimidine compounds by hydrazine hydrate [3], led to a further investigation of the behavior of the quinazolinone ring in relation to hydrolytic agents.

The present communication gives cases of pyrimidine ring opening taking place on hydrazinolysis of 2-R-quinazol-4-ones, R=H, I; R=CH₃, II; R=C₆H₅, III. Hydrazinolysis was effected by refluxing the indicated compounds with 10-15-fold excess hydrazine hydrate, for five hours, in the case of compounds I and II, and 12 hrs, in the case of compound III.

Quinazalone I gave a 68% yield of anthranilic acid hydrazide, mp 120-121° [4]. Found: C 55.70; H 6.23; N 27.97%. Calculated for C₇H₉N₃O: C 55.99; H 5.99; N 27.81%.

Quinazalone II gave a 73% yield of 2-methyl-3-aminoquinazol-4-one, mp 150° [5]. Found: C 61.74; H 5.22; N 24.15%. Calculated for C₉H₉N₃O: C 61.71; H 5.14; N 24.00%.

Hydrazinolysis of quinazalone III gave a 37% yield of 2-phenyl-3-aminoquinazol-4-one, mp 178-179° [5]. Found: C 70.95; H 4.75%. Calculated for C₁₄H₁₁N₃O: C 70.88; H 4.63%. Furthermore, 20% of the starting quinazalone was recovered. The structures of all compounds prepared were confirmed by analysis, mixed mp, and comparison of the ir spectrum (region 1700-700 cm⁻¹) with those of products of known structure, synthesized by the methods of [4] and [5]. Hydrazinolysis can be represented as



The hydrazinolysis reactions described are a new case of opening of the pyrimidine ring of a quinazol-4-one*. With compounds II and III the intermediate A** closes again to quinazalone, with entry of hydrazine hydrate into the ring of IV, V. With compound I, where R = H, the unstable intermediate A hydrolyzes to anthranilic acid hydrazide VI.

REFERENCES

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3. F. Baumbach, H. G. Henning, and G. Hilgetag, *Z. Chem.*, 4, 67, 1964.
4. Th. Curtius, *J. pr. Chem.*, [2] 81, 523, 1910.

*A similar case of hydrazinolysis, resulting in formation of 3-aminoquinazolinone-2,4-dione from quinazolinone-2,4-dione was described in [6].

** The structure of the assumed intermediate product A and the reaction mechanism need more precise definition.