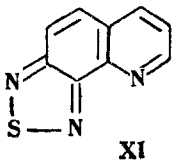
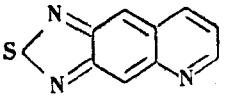


XI



XII

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Leningrad Chemical-Pharmaceutical Institute

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HYDRAZINOLYSIS OF SOME QUINAZOLONES

S. L. Mertsalov, N. N. Vereshchagina, and I. Ya. Postovskii

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

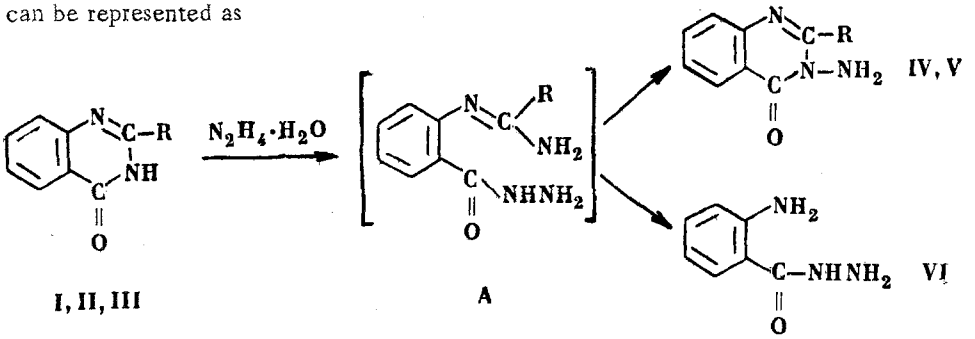
It is known that 2-aryl-3-aroylamidoquinazol-4-ones undergo opening of the pyrimidine ring when heated with dilute aqueous alkali, giving substituted triazoles [1]. Not long ago the present authors [2] described a case of opening of the pyrimidine ring of 1-(2'-R-quinazolyl)-4-phenylthiosemicarbazides 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 quinazoline 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=CH_3, II; R=C_6H_5, 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.

Quinzalone 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 $C_7H_9N_3O$: C 55.99; H 5.99; N 27.81%.

Quinazolone 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 $C_9H_9N_3O$: C 61.71; H 5.14; N 24.00%.

Hydrazinolysis of quinazolone 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 $C_{14}H_{11}N_3O$: C 70.88; H 4.63%. Furthermore, 20% of the starting quinazolone 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



I, II, III — A — IV, V — VI

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 quinazolone, 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.

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

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

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SYNTHESIS OF IMIDAZO[1, 2-a]BENZIMIDAZOLE AND IMIDAZOLINO[1, 2-a]-BENZIMIDAZOLE DERIVATIVES

A. M. Siminov, and P. M. Kochergin

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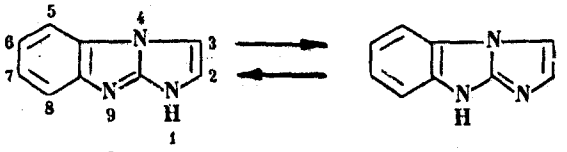
The imidazo[1, 2-a]benzimidazole (I) system is practically unexplored. The preparation of only two compounds



I

2, 3-diphenylamidazo[1, 2-a]benzimidazole (structure not precisely ascertained) [1] and 1-ethyl-7-nitro-2, 3-dihydroimidazole[1, 2-a]benzimidazole [2], has been described. Using the literature methods of closing imidazole [3-5] and imidazoline [6, 7] rings, and applying them to 2-amino-heterocyclics we synthesized a number of substituted derivatives of the tricyclic system I and its 2, 3-dihydro- derivatives. The reaction of 1-alkyl-2-aminobenzimidazoles with α-halogenoketones and α-halogenoalcohols led to the preparation of the corresponding 1, 3-disubstituted 2-iminobenzimidazolines. On treatment with dehydrating agents, the latter, by heating with mineral or organic acids, are made to split off a molecule of water and cyclize to derivatives I or the corresponding 2, 3-dihydro- compounds.

1-Ethyl-3-phenacyl-2-iminobenzimidazoline. Mp 120.5° (from aqueous CH_3OH). Found: C 73.35; H 6.02; N 15.08%. Calculated for $C_{17}H_{17}N_3O$: C 73.10; H 6.14; N 15.04%.

Hydrobromide. Mp 222-222.5° (decomp., from CH_3OH). Found: Br 22.06%. Calculated for $C_{17}H_{17}N_3O$: Br 22.19%.

2-Phenyl-9-ethylimidazo(1, 2-a)benzimidazole. Mp 93-93.5° (from aqueous alcohol). Found: C 77.93; H 5.57; N 16.19%. Calculated for $C_{17}H_{15}N_3$: C 78.13; H 5.79; N 16.08%.

Picrate. Mp 238-240° (decomp., from alcohol). Found: C 56.57; H 3.73; N 17.02%. Calculated for $C_{17}H_{15}N_3 \cdot C_6H_3N_3O_7$: C 56.33; H 3.70; N 17.14%.

1-Ethyl-3-β-hydroxyethyl-2-iminobenzimidazoline. Mp 122.5-123° (from dichloroethane). Found: C 65.08; H 7.47; N 20.28%. Calculated for $C_{11}H_{15}N_3O$: C 64.37; H 7.37; N 20.47%.

Hydrobromide. Mp 226.5-227° (decomp., from alcohol). Found: Br 28.15%. Calculated for $C_{11}H_{15}N_3O \cdot HBr$: Br 27.92%.

Picrate. Mp 182-183° (from water). Found: N 19.33%. Calculated for $C_{11}H_{15}N_3O \cdot C_6H_3N_3O_7$: N 19.35%.

9-Ethylimidazolino(1, 2-a)benzimidazole. Picrate, mp 267-268° (decomp., from CH_3COOH). Found: C 48.96; H 3.90; N 20.02%. Calculated for $C_{11}H_{13}N_3 \cdot C_6H_3N_3O_7$: C 49.04; H 3.87; N 20.19%.

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