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SHORT COMMUNICATIONS

Reactions of Ethyl 1-Benzylidene-7a-hydroxy-4-phenyl-6-oxo-octahydro-1*H*-indene-5-carboxylate and Ethyl 5-Benzylidene-4a-hydroxy-1-phenyl-3-oxodecahydronaphthalene-2-carboxylate with 1,2,4-Triazol-3-amine. Synthesis of Substituted Triazoloquinazolines

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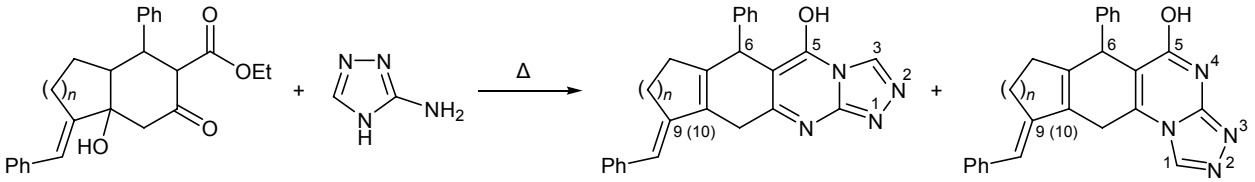
Due to the presence of several reaction centers, hydroxy oxo derivatives of octahydroindene and decahydronaphthalene may be used as intermediate products in the synthesis of various complex systems. The 1,3-dicarbonyl fragment in their molecules is capable of being involved in heterocyclizations with difunctional nucleophiles. Reactions of such compounds with hydrazine and hydroxylamine were studied in sufficient detail [1]. However, only a few data are available on reactions of their analogs, hydroxyoxocyclohexanecarboxylates, with 3-amino-1,2,4-triazole [2]; the product structure was thoroughly studied using 2D NMR spectroscopy.

In the present communication we report on the reactions of ethyl 1-benzylidene-7a-hydroxy-6-oxo-4-phenyloctahydro-1*H*-indene-5-carboxylate (**I**) and ethyl 5-benzylidene-4a-hydroxy-3-oxo-1-phenyldecahydronaphthalene-2-carboxylate (**II**) with 3-amino-1,2,4-triazole. The presence of several reaction centers in the substrate and reagent could give rise to formation of systems with different modes of ring fusion and different positions of heteroatoms.

By heating equimolar amounts of the reactants at 140–160°C under solvent-free conditions we obtained previously unknown fused triazoloquinazoline derivatives: 9-benzylidene-6-phenyl-7,8,9,10-tetrahydro-6*H*-cyclopenta[*g*][1,2,4]triazolo[3,4-*b*]- and -[4,3-*a*]quinazolin-5-ols **IIIa** and **IIIb** and 10-benzylidene-6-phenyl-6,7,8,9,10,11-hexahydrobenzo[*g*][1,2,4]triazolo[3,4-*b*]- and -[4,3-*a*]quinazolin-5-ols **IVa** and **IVb** (Scheme 1). The ^{1}H NMR spectra of the product mixtures contained double sets of signals from benzylic [6-H, δ 4.68 (**IIIa**), 4.62 (**IIIb**), 4.47 (**IVa**), 4.41 ppm (**IVb**)] and vinylic protons [9-CH, δ 6.18 (**IIIa**), 6.35 ppm (**IIIb**); 10-CH, δ 6.48 (**IVa**), 6.62 ppm (**IVb**)]. Signals were assigned to the linear and angular isomers with account taken of magnetic anisotropy of the triazole ring.

We succeeded in identifying only signals from major isomers **IIIa** and **IVa** in the ^{13}C NMR spectra of

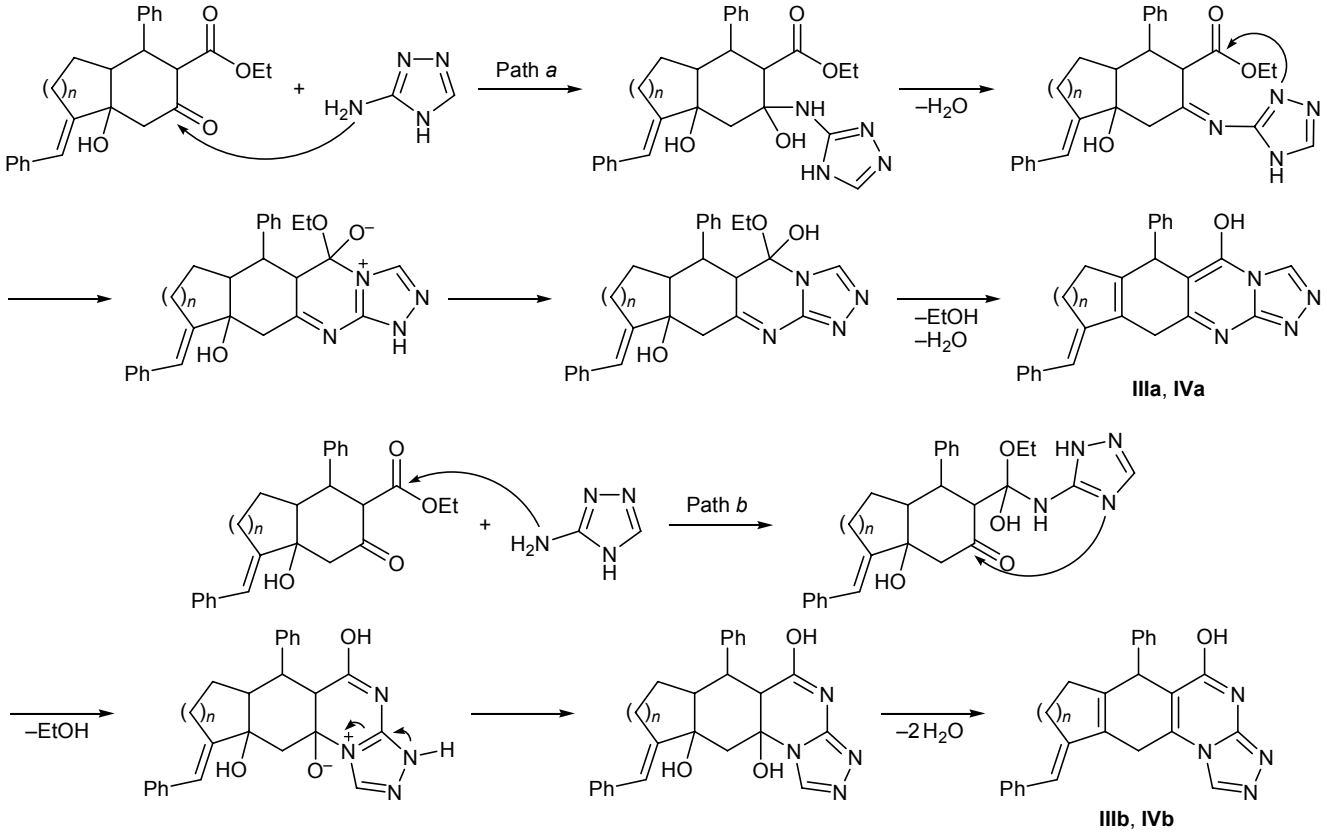
Scheme 1.



I, **II** **IIIa**, **IVa** **IIIb**, **IVb**

I, **III**, $n = 1$; **II**, **IV**, $n = 2$.

Scheme 2.



the product mixtures. The spectra contained, respectively, four and five signals from sp^3-carbon atoms, which indicated that the heterocyclization was accompanied by dehydration.

A probable scheme of formation of isomeric linearly and angularly fused triazoloquinazoline derivatives involves initial nucleophilic attack by the primary amino group of aminotriazole at the ketone (path *a*) or ester carbonyl group (path *b*) in the substrate. The subsequent attack by the pyridine-type nitrogen atom in the triazole fragment on the other carbonyl carbon atom leads to the corresponding intramolecular cyclization products (Scheme 2).

Heterocyclic systems **III** and **IV** consist of four fused rings, and they can be regarded as structural analogs of tetracycline antibiotics. Therefore, we plan to separate the obtained mixtures of isomers with a view to examine their biological activity.

9-Benzylidene-6-phenyl-7,8,9,10-tetrahydro-6*H*-cyclopenta[*g*][1,2,4]triazolo[3,4-*b*]quinazolin-5-ol (IIIa) and 9-benzylidene-6-phenyl-7,8,9,10-tetrahydro-6*H*-cyclopenta[*g*][1,2,4]triazolo[4,3-*a*]quinazolin-5-ol (IIIb). A mixture of 1 g (2.6 mmol) of ester **I** and 0.22 g (2.6 mmol) of 3-amino-1,2,4-triazole was heated for 60 min at 140–160°C. The crystalline product was washed with water and ethanol. Overall yield 0.67 g (66%), light-yellow crystals, mp 242–260°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 4.68 s and 4.62 s (1H, 6-H), 5.79 br.s (5-OH), 6.18 s and 6.35 s (1H, 9-CH), 7.14–7.42 m (10H, H_{arom}), 8.14 s and 8.16 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 26.82 (C^7), 29.90 (C^8), 32.05 (C^{10}), 43.21 (C^6), 152.48 (C^3). Found, %: C 76.01; H 5.44; N 14.48. $C_{25}H_{20}N_4O$. Calculated, %: C 76.51; H 5.14; N 14.28.

10-Benzylidene-6-phenyl-6,7,8,9,10,11-hexahydrobenzo[*g*][1,2,4]triazolo[3,4-*b*]quinazolin-5-ol (IVa) and 10-benzylidene-6-phenyl-6,7,8,9,10,11-hexahydrobenzo[*g*][1,2,4]triazolo[4,3-*a*]quinazolin-5-ol (IVb) were synthesized in a similar way. Yield 63%, mp 227–237°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 4.47 s and 4.41 s (1H, 6-H), 5.65 br.s (5-OH), 6.48 s and 6.62 s (10-CH), 7.13–7.34 m (10H, H_{arom}), 8.09 s and 8.11 s (1H, 1-H). ^{13}C NMR spectrum, δ_C, ppm: 22.76 (C^8), 27.29 (C^7), 29.11 (C^9), 29.23 (C^{11}), 46.67 (C^6), 152.24 (C^3). Found, %: C 76.53; H 5.75; N 13.92. $C_{26}H_{22}N_4O$. Calculated, %: C 76.83; H 5.46; N 13.78.

The ^1H and ^{13}C NMR spectra were recorded on a Varian spectrometer at 400 MHz (for ^1H) using DMSO-d_6 as solvent and TMS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates [C_6H_{14}–(i-Pr)$_2$O–$CHCl_3$, 3 : 1 : 1]; spots were visualized by treatment with iodine vapor or water.

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